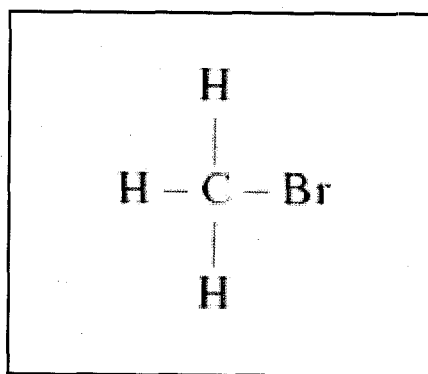




Office of Prevention, Pesticides,
and Toxic Substances

**Environmental Fate and Ecological Risk Assessment
for the Re-registration of Methyl Bromide**



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TABLE OF CONTENTS

TABLE OF CONTENTS	i
LIST OF TABLES	ii
LIST OF FIGURES	iv
LIST OF APPENDICES	v
LIST OF ACRONYMS	vi
CONVERSION FACTORS	vii
I. EXECUTIVE SUMMARY	1
II. INTRODUCTION	2
(A) Problem Formulation	2
(B) Mode of Action	5
(C) Use Data	5
III. INTEGRATED ENVIRONMENTAL RISK CHARACTERIZATION	8
(A) Environmental Fate Summary	8
(B) Ecological Risk Summary	9
(C) Endangered Species	12
(D) Endocrine Disruption	13
IV. ENVIRONMENTAL FATE AND TRANSPORT CHARACTERIZATION	14
(A) Physical, Chemical, and Environmental Fate properties of Methyl Bromide	14
(B) Transport and Partitioning	16
(i) Volatilization	16
(ii) Adsorption	18
(C) Persistence	19
(i) Degradation In Air	19
(ii) Degradation In Water	20
(iii) Degradation In Soil	22
(iv) Lifetime Of Methyl Bromide	24
(D) Ozone Depletion Potential	24
(E) Global Warming Potential	25
(F) Environmental Levels of Methyl Bromide	26
(i) Methyl Bromide Concentrations in Air	26
(ii) Estimated Methyl Bromide Concentrations in Air	32
(iii) Bromide Ion Concentrations in Soil and Sediment	34

TABLE OF CONTENTS (continued)

V. WATER RESOURCE ASSESSMENT	36
(A) Tier I/II PRZM/EXAMS and FIRST Modeling (Surface Water)	36
(i) Estimated Drinking Water Concentration of methyl bromide	38
(ii) Estimated Drinking Water Concentration of bromide ion	38
(iii) Groundwater Monitoring Data for Drinking Water Assessment	39
(iv) Estimated Environmental Concentration of Methyl Bromide for Ecological Risk Assessment	41
(v) Estimated Environmental Concentration of Bromide Ion for Ecological Risk Assessment	41
(B) Monitoring Data - Methyl Bromide and Bromide Ion Concentrations in Water	42
(i) Surface Water	42
(ii) Ground Water	43
VI. ECOLOGICAL HAZARD DATA	44
(A) Summary	44
(B) Effects in Target Organisms	48
(C) Toxicity to Terrestrial Animals	48
(i) Mammals, Acute and Subacute	49
(ii) Birds, Acute and Subacute	49
(iii) Invertebrates	50
(D) Toxicity to Other Terrestrial Species	51
(i) Macrophytes	51
(ii) Microorganisms	51
(E) Toxicity to Aquatic Species	52
(i) Freshwater Fish, Acute and Chronic	52
(ii) Freshwater Invertebrates, Acute and Chronic	53
(iii) Algae and Macrophytes	53
VII. AQUATIC AND TERRESTRIAL EXPOSURE AND RISK ASSESSMENT	54
(A) Terrestrial Organisms	56
(i) Risk to Mammals	56
(ii) Risk to Birds	57
(B) Aquatic Organisms	58
(i) Methyl Bromide	58
(ii) Bromide Ion	59
ACKNOWLEDGMENT	60
REFERENCES	61

LIST OF TABLES

Table 1. Physical, Chemical, and Environmental Fate Properties of Methyl Bromide	14
Table 2 Hydrolysis half-life of methyl bromide	21
Table 3. Direct GWP for some CFCs, HCFCs, and methyl bromide	26
Table 4. Ambient air concentrations of methyl bromide	27
Table 5. Ambient air concentrations in parts per billion near areas of methyl bromide use	28
Table 6. Air concentrations of methyl bromide from chamber/field fumigations.	29
Table 7. Methyl bromide concentrations following fumigation of a greenhouse	31
Table 8. Methyl bromide concentrations during and immediately following fumigation at an agricultural field	32
Table 9. PRZM/EXAMS Input Parameters for Methyl Bromide	37
Table 10. FIRST Input Parameters for Methyl Bromide	39
Table 11. Methyl bromide and bromide ion in surface water and groundwater	40
Table 12. Surface water EECs ($\mu\text{g/L}$) for ecological risk assessment based on methyl bromide use on various crops	40
Table 13. Surface water EECs ($\mu\text{g/L}$) of bromide ion for ecological risk assessment based on use methyl bromide use in North Carolina Tobacco.	42
Table 14. Concentrations of methyl bromide or the bromide ion in surface waters	43
Table 15. Summary of toxicity values for methyl bromide	45
Table 16. Comparison of toxicity values for methyl bromide and bromide ion in aquatic species	47
Table 17. Summary of toxicity values for bromide ion	48
Table 18. Risk presumptions for terrestrial animals based on risk quotient (RQ) and levels of Concern (LOC)	54

LIST OF TABLES (continued)

Table 19. Risk presumptions for aquatic animals based on risk quotient (RQ) and levels of Concern (LOC)	55
Table 20. Risk presumptions for plants based on risk quotient (RQ) and levels of Concern (LOC)	55
Table B1. Methyl bromide sources and sinks	B-3
Table E1. Risk Quotients for methyl bromide for inhalation exposure of mammals	E-1
Table E2. Risk Quotients for Inhalation Exposure of Birds Using the LD ₅₀ /ft ² Risk Assessment Method	E-1
Table E3. Risk Quotients for Inhalation Exposure of Birds Using field monitoring data ...	E-2
Table E4. Risk Quotients for Inhalation Exposure of Birds Using ISCST model estimated data	E-2
Table E5. Risk Quotients for methyl bromide acute and chronic exposures of aquatic species	E-3
Table E6. Risk Quotients for methyl bromide acute exposures of algae	E-4

LIST OF FIGURES

Figure 1. Map of methyl bromide use as pesticide in the United States	7
Figure 2. Selected ISCST estimated methyl bromide concentrations under various emission rates, field sizes, and application methods..	34
Figure B1: Hydroxyl radical concentration as a function of time	B-1
Figure B2. Probability density function for the atmospheric half-life of methyl bromide in the Northern and Southern Hemisphere	B-1
Figure B3. Cumulative distribution function for the atmospheric half-life of methyl bromide in the Northern and Southern Hemisphere	B-2

LIST OF APPENDICES

Appendix A: Effects Data

Appendix A1: Effects Data: Toxicity of Methyl Bromide to Terrestrial Animals

Appendix A2: Effects Data: Toxicity of Methyl Bromide to Aquatic Species

Appendix A3: Effects Data: Toxicity of Methyl Bromide to Terrestrial Plants

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide

Appendix A5: Effects Data: Toxicity of Bromide Ion

Appendix B: Environmental Fate Data

Appendix C: Modeling Inputs/Outputs for Ecological and Drinking Water Risk Assessment

Appendix D: Groundwater and Surface Water Concentrations of Methyl Bromide and Bromide,
United States Geological Survey National Water Quality Assessment

Appendix E: Detailed Risk Quotients

Appendix F: HED DOC. NO. 0051439. Methyl Bromide - 2nd Report of the Health Effects
Division (HED) Hazard Identification Assessment Review Committee (HIARC)

NOTE: Appendices are placed after the Reference Section

ACRONYMS

a.i.	Active Ingredient
ALE	Atmospheric Lifetime Experiment
ATSDR	Agency for Toxic Substances and Disease Registry
CAM	Chemical Application Method
CAS	Chemical Abstracts Service
CDF	Cumulative Distribution Function
CDPR	California Department of Pesticide Regulation
CFC	Chlorofluorocarbon
CUE	Critical Use Exemption
EDWC	Estimated Drinking Water Concentration
EDSP	Endocrine Disruption Screening Program
EDSTAC	Endocrine Disruption Screening Testing Advisory Committee
EEC	Estimated Environmental Concentration
EFED	Environmental Fate and Effects Division
EIIS	Ecological Incident Information System
EXAMS	Exposure Analysis Modeling System
FEAD	Field and External Affairs Division
FFDCA	Federal Food, Drug, and Cosmetic Act
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
FIRST	FQPA (Food Quality Protection Act) Index Reservoir Screening Tool
FQPA	Food Quality Protection Act
GAGE	Global Atmospheric Gases Experiment
GENEEC	Generic Estimated Environmental Concentration
GWP	Global Warming Potential
HED	Health Effects Division
HDPE	High Density Polyethylene
HIARC	Hazard Identification Assessment Review Committee
IARC	International Arctic Research Center
IRSD	Information Resources and Services Division
ISCST	Industrial Source Complex - Short Term
LC ₅₀	Median Lethal Concentration
LD ₅₀	Median Lethal Dose
LOAEL	Lowest Observed Adverse Effect Level
LOC	Level of Concern
MARC	Metabolism Assessment Review Committee
mg/kg	Milligram Per Kilogram
mg/L	Milligrams Per Liter
MOE	Margin of Exposure
MRID	Master Record Identification (number)
NAWQA	USGS National Water Quality Assessment
NOAEL	No Observed Adverse Effect Level
NOAEC	No Observed Acute Effect Concentration
ODP	Ozone Depletion Potential
OPP	Office of Pesticide Programs in EPA
OPPTS	Office of Prevention, Pesticides and Toxic Substances in EPA
PCA	Percent Crop Area
PDF	Probability Distribution Function
ppb	Parts Per Billion
ppm	Parts Per Million
PRZM	Pesticide Root Zone Model

ACRONYMS

RED	Reregistration Eligibility Decision
RfD	Reference Dose
RQ	Risk Quotient
SCI-GROW	Screening Concentrations In Ground Water Model
SRRD	Special Review and Reregistration Division
TGAI	Technical Grade Active Ingredient
TRU	Toxicity Reference Value
µg/g	Micrograms Per Gram
µg/L	Micrograms Per Liter
µg/m ³	Micrograms Per Cubic meter
UNEP	United Nations Environmental Program
USDA	United States Department of Agriculture
USEPA	U.S. Environmental Protection Agency
USFWS	United States Fish and Wildlife Service
USGS	United States Geological Survey
WHO	World Health Organization
WMO	World Meteorological Organization

CONVERSION FACTORS

To convert concentrations in air (at 25 °C) from ppm to mg/m³: $\text{mg/m}^3 = (\text{ppm}) \times (\text{molecular weight of the compound}) / (24.45)$. For methyl bromide: 1 ppm = 3.9 mg/m³.

To convert concentrations in air from µg/m³ to mg/m³: $\text{mg/m}^3 = (\mu\text{g/m}^3) \times (1 \text{ mg} / 1,000 \mu\text{g})$.

I. EXECUTIVE SUMMARY

Methyl bromide is a widely used fumigant on agricultural sites as a preplant soil sterilant to control nematodes, soil-borne diseases, insects and weeds. The high vapor pressure (1620 mm) and low affinity for sorption (K_{oc} 32.0 L kg⁻¹) on soil of methyl bromide suggest that volatilization is the most important environmental route of dissipation and to a lesser extent leaching and degradation. The most recent estimate for the total lifetime of atmospheric methyl bromide is approximately 0.7 years, which leads to an Ozone Depletion Potential (ODP) of about 0.38. Methyl bromide has been identified as a significant ozone depleting substance.

Inhalation of methyl bromide vapor following soil fumigation is considered to be the major route of exposure for terrestrial organisms. An analysis using mammal inhalation data, estimated bird inhalation data, monitoring data, and the air dispersion model estimated edge-of-field air concentrations of methyl bromide does not appear to indicate a potential acute concern. Avian inhalation toxicity data are needed for a complete assessment. There is also a potential for exposure over a prolonged period. Birds and mammals could have territories or home ranges in the area and be exposed continuously or repeatedly, due to the use of methyl bromide on multiple fields over multiple days in any given geographic area. Chronic inhalation toxicity data would be needed to address this potential exposure.

For aquatic organisms, exposure in surface water could result from runoff with soluble methyl bromide from fumigated fields. Based on PRZM/EXAMS modeling of methyl bromide, the only aquatic LOC exceeded is the acute endangered species LOC for aquatic invertebrates. The acute aquatic endangered species LOC (0.05) is exceeded for aquatic invertebrates in two of the four modeled scenarios (CA tomatoes, 0.06 and FL strawberries, 0.07), but not with CA grapes or NC tobacco. However, the PRZM model does not account for the reduction in exposure that would likely result from tarping the field immediately after methyl bromide application. Given the low levels of exceedence (RQs of 0.06 to 0.07), the potential effect of tarping might lower the RQs values below the LOC. Acute and chronic fish LOCs are not exceeded, but these are based only on supplemental and/or literature data. Chronic aquatic invertebrate data are needed to evaluate chronic risk from methyl bromide. However, the Henry's Law Constant of 744 Pa-m³/mol suggests that it will be volatilized from surface water, thus chronic exposure to methyl bromide is expected to be low. Also, the low octanol/water partition coefficient of methyl bromide indicates that it is not likely to be bioconcentrated in tissues of aquatic organisms.

Based on the available efficacy data and labeling, non-target plants off-site will likely also be at some risk from off-gassed methyl bromide. Terrestrial plant toxicity data are needed to evaluate this risk. Level of concerns for aquatic plants are not exceeded based on available data, but additional toxicity data are needed to complete this assessment.

Monitoring data for the bromide ion (major degradate of methyl bromide) includes several values above the available literature NOAEC for adverse effects on reproduction in both fish and aquatic invertebrates. However, bromide concentrations in the monitoring data are not associated

with a soil fumigation of methyl bromide; thus, it is unclear how these concentrations would correspond to water contaminated with methyl bromide runoff from a nearby field or to exposures scenarios for aquatic receptors. Therefore, Tier I GENEEC model was used in estimating bromide ion EECs. The maximum chronic concentration for the modeled pond was slightly below the chronic endpoints based on open literature data. Guideline chronic ecological effects data on the bromide ion are needed for a complete assessment and to reduce uncertainty.

II. INTRODUCTION

Methyl bromide is a colorless and odorless gas at room temperature and atmospheric pressure. It is commercially available as a liquified gas that uses as a broad spectrum fumigant extensively on a global basis against nematodes, weeds, insects, fungi, bacteria, and rodents. Approximately 60 million pounds of methyl bromide are used annually in the United States of America (USA). Methyl bromide has been identified as a significant ozone depleting substance, resulting in regulatory actions being taken by the U.S. Environmental Protection Agency under the Clean Air Act and by the United Nations Environment Program (Montreal Protocol). Under the Clean Air Act and the Montreal Protocol, the production and importation of methyl bromide will be phased out in the United States on January 1, 2005. Citing lack of technically and economically feasible alternatives, which have taken longer than anticipated to develop, methyl bromide is seen by the USA consumers as an essential pesticide for a number of crops production. The Critical Use Exemption (CEU) program of the Montreal Protocol allows limited production and importation of methyl bromide beyond the phase-out date for specific uses. The U.S. Government has submitted CEUs for selected uses of methyl bromide under the "phase-out" program of the Montreal Protocol. This document is prepared to evaluate the environmental fate and ecological risk of methyl bromide in support of the reregistration eligibility decision (RED) on methyl bromide for its continuing use as a pre-plant fumigation of soils.

(A) Problem Formulation

In general, the analysis plan and rationale for completing this assessment, *i.e.*, the problem formulation, have been to determine whether current label uses of methyl bromide may result in exposure that could represent an unreasonable likelihood of adverse effects (risk) to nontarget endangered/threatened and non-endangered animals and plants that could potentially impact the reregistration eligibility decision under the Federal Insecticide, Fungicide and Rodenticide Act, the Food Quality Protection Act, and the Endangered Species Act. Both registrant-submitted guideline data and information collected from the open literature were considered to characterize the environmental fate and ecological effects of methyl bromide and its primary degradation product in water, the bromide ion. A risk quotient (RQ) approach is used whereby the ratio of exposure concentration to effects concentration is compared against a level of concern (LOC). This is a screening-level deterministic assessment. Although risk, in the context intended here, is often defined as the likelihood and magnitude of adverse ecological effects, the deterministic RQ approach does not provide a quantitative estimate of likelihood and/or magnitude of an adverse effect.

Methyl bromide is used as a soil and space fumigant to control fungi, nematodes, weeds, and rodents. This ecological risk assessment considers maximum application rates on vulnerable soils for representative crops to estimate exposure concentrations. This assessment is not intended to represent a site- or time-specific analysis. Instead, this assessment is intended to represent a national level exposure based on vulnerable soils. Likewise, the most sensitive toxicity endpoints are used from surrogate test species to estimate treatment-related direct effects on acute mortality and chronic reproductive, growth and survival assessment endpoints. Toxicity tests are intended to determine effects of pesticide exposure on birds, mammals, fish, terrestrial and aquatic invertebrates, and plants. These tests include short-term acute, subacute and reproduction studies and are typically arranged in a hierarchical or tiered system that progresses from basic laboratory tests to applied field studies. The toxicity studies are used to evaluate the potential of a pesticide to cause adverse effects, to determine whether further testing is required, and to determine the need for precautionary label statements to minimize the potential adverse effects to nontarget animals and plants (CFR 40 §158.202, 2002).

The conceptual model used to depict the ecological risk associated with methyl bromide was initially fairly generic and assumed that as a pesticide, methyl bromide was capable of affecting terrestrial and aquatic animals provided environmental concentrations were sufficiently elevated as a result of labeled uses. Pesticide exposures can occur through multiple routes, including inhalation, dermal contact, and ingestion of contaminated water or vegetation. However, through an iterative process of examining fate and effects data, including environmental monitoring data, the conceptual model has been refined to reflect the exposure pathways and the organisms for which risk is greatest. Since methyl bromide is highly volatile and is a gas at room temperature and standard pressure, the major exposure pathway for mammals and birds is considered to be inhalation of methyl bromide vapor following soil fumigation. Mammals and birds could also be exposed to methyl bromide through ingestion of water contaminated by runoff from agricultural fields as well as dermal absorption; however, relative to the inhalation exposure route, exposure via contaminated drinking water or dermal absorption are likely to be very minor. It is also possible that mammals and birds could be exposed to methyl bromide through ingestion of methyl bromide residues on plant materials. However, since no data are available to estimate methyl bromide residues on plants, this exposure pathway is not considered. For aquatic receptors, exposure could result through surface water contaminated with runoff from agricultural fields.

The efficacy of methyl bromide has been well studied. Several reviews of the environmental fate of methyl bromide and the effects of methyl bromide in laboratory and other species are available (ATSDR 1992, U.S. EPA 1986, 2003, WHO 1995). It has a broad spectrum of activity and has toxic effects in both target and non-target species. Comprehensive reviews of the toxicity of methyl bromide to laboratory mammals and humans are available (ATSDR 1992, WHO 1995). The ecotoxicity database on terrestrial and aquatic organisms for methyl bromide was reviewed for this assessment, including both MRID submissions and studies from the open literature. Toxicity databases for acute exposure of mammals, birds, fish, aquatic invertebrates and algae and chronic exposure of mammals and fish are adequate to estimate risk using a RQ approach.

In addition to target soil organisms, methyl bromide also eradicates soil flora, protozoa, gastropods and arachnids. There is a large variation in tolerance of insects to methyl bromide, even in different strains of the same species (WHO 1995, Bell 1988). Regarding effects on terrestrial plants, methyl bromide has a broad spectrum of phytotoxic effects, ranging from delayed seed germination to plant death. There is a large variation in tolerance of plants to methyl bromide, with leafy vegetables being the most sensitive (WHO 1995). The available data on the effects of methyl bromide exposure in non-target terrestrial invertebrates, microorganisms, and terrestrial and aquatic plants are not adequate for quantitative risk assessment and risks are only characterized qualitatively.

Risks to mammals from inhalation exposure to methyl bromide vapor are based on monitoring data and available inhalation toxicity data in mammals. For birds, results of a single acute gavage study suggest that methyl bromide is moderately toxic to bobwhite quail (MRID 43085901); no additional information regarding the toxicity of methyl bromide to avian species is available. The LD_{50}/ft^2 method was used as a rough risk calculation screen for mammals and birds. This was refined in the risk characterization using methyl bromide concentrations in air, including those estimated by the Industrial Source Complex - Short Term (ISCST) air dispersion model. Risk to aquatic species was based on estimated environmental concentrations (EECs) using the Pesticide Root Zone Model (PRZM) linked to the Exposure Analysis Model (EXAMS) combined with the available toxicity data in aquatic species.

In soil and water, methyl bromide is degraded by a combination of abiotic and biotic processes, and the rate of these reactions influences the amount of methyl bromide that is ultimately volatilized to the atmosphere. The primary degradation products are methanol and the bromide ion. As an element, the bromide ion may persist longer in water than methyl bromide, potentially resulting in the accumulation of the bromide ion in water. Thus, exposure to the bromide ion in aquatic species was also considered. Risk to aquatic species from the bromide ion was based on monitoring data, Tier I GENEEC (Generic Estimated Environmental Concentration) model generated EECs, and available toxicity data in aquatic species. Methanol was detected only in the hydrolysis studies. Methanol is a ubiquitous compound and has been identified as a natural emission product from various plants and as a biological decomposition product of natural waste and sewage. Methanol is also a common solvent, frequently used in pesticide formulations. Methanol is completely miscible in water and it has vapor pressure of 92 mm Hg and Henry's Law Constant of $0.45 \text{ Pa}\cdot\text{m}^3/\text{mol}$ at 25.0°C , which suggests it will be volatilized from water bodies in the natural environment. Because of the above factors, the present assessment focuses on the parent methyl bromide and degradate bromide ion.

Methyl bromide is a naturally occurring contaminant of air and water, with oceans as the most likely natural source of methyl bromide. The primary non-natural source of methyl bromide in the environment is that released into the atmosphere by fumigation and, to a lesser extent, by automobile exhaust. Because methyl bromide has a high potential for volatilization and tends to partition to the atmosphere where it is slowly degraded, the ozone depletion potential and global

warming potential associated with agricultural uses of methyl bromide are also presented in this assessment. The half-life for the degradation by hydroxyl radicals is less than one year, but is greatly dependent upon the atmospheric hydroxyl radical concentration. Methyl bromide that has not degraded in the troposphere will gradually diffuse into the stratosphere above the ozone layer where it will slowly degrade due to direct photolysis from UV-C radiation and contribute to the catalytic removal of stratospheric ozone. A qualitative assessment of recent trends of methyl bromide in the atmosphere is presented. The ecological risk assessment related to the ozone depletion potential is beyond the scope of this risk assessment, but is briefly discussed qualitatively.

(B) Mode of Action

The mechanism of toxicity of methyl bromide has not been proven. It has been proposed that the toxic effects of methyl bromide in animal species are due direct cytotoxic actions of methyl bromide or a methyl bromide metabolite, possibly through alkylation of proteins (WHO 1995). In terrestrial mammals, central nervous system toxicity appears related to the incorporation of methyl bromide or the methyl moiety into tissues (WHO 1995). In fish, methyl bromide exposure results in dose-related degenerative effects to the epithelia of gills and the oral mucosa (Webster et al. 1998, Webster and Vos 1994), which ultimately lead to death due to suffocation (Segers et al. 1984). Although the mechanism of toxicity in fish had not been proven, morphological damage to gills and mucosal membranes are indicative of alkylation of cell membranes (Segers et al. 1984). No mechanism of toxicity of methyl bromide has been established or proposed for other aquatic species. There is no proven mechanism for the phytotoxic effects of methyl bromide, although it has been proposed that excessive accumulation of bromide ion by plants produces many of the toxic effects (WHO 1995). In carnation plants exposed to methyl bromide by soil fumigation, plant survival and flower yield were inversely proportional to inorganic bromide concentration of soil (Kempton and Maw 1974). However, it is also possible that some of the phytotoxic effects of methyl bromide are due to indirect actions, such as the elimination of beneficial microorganisms from soil (MRID 00118842, Lambert et al. 1979).

(C) Use Data

Methyl bromide is a colorless, odorless gas at room temperature and standard pressure; it is soluble in water. Methyl bromide is used as a soil fumigant in fields and greenhouses. It can be applied using several methods, including augering, back-hoe, chisel, hot gas, raised tarp, and soil injection (Great Lakes Chemical Corporation). Deep soil injection and tarping methods can be used to minimize emissions. For space fumigation, injection and recirculation are the most common application methods. Commercial formulations of methyl bromide for agricultural use are available as pressurized liquid or gas and may contain chloropicrin or amyl acetate as odorants. Formulations for soil fumigation usually contain 2% chloropicrin or 0.3% amyl acetate (WHO 1995). Other formulations include up to 70% chloropicrin or other fumigants or hydrocarbons as inert diluents. For commodity fumigation, 100% methyl bromide is used (WHO

1995). Application rates vary greatly, depending upon the type and extent of infestation, crop type, soil type and application method. Application rates for methyl bromide as a soil fumigant are typically 50 to 100 g/m² (446-892 lbs/acre)(WHO 1995). California limits the maximum application rate of methyl bromide for agricultural crops to 400 lbs/acre.

Subsurface shank injection of methyl bromide application is the most common method of soil fumigation. In general, methyl bromide is injected into soil at a certain depth (6 to 18 inches) using a positive pressure and immediately followed by covering with polyethylene tarp to prevent methyl bromide escaping. Also, methyl bromide can be applied without covering with polyethylene tarp when it is injected to a depth of up to 18 inches. In addition, the "hot gas method" of methyl bromide application consists of introducing hot water prior to methyl bromide injection to enhance the volatilization of methyl bromide from the treated field. However, in California, the application of methyl bromide as hot gas is through a subsurface drip irrigation system to tarpaulin-covered beds and limited to a maximum of 225 pounds per acre application rate.

For post-harvest and stored commodity fumigation (space fumigation), typical application rates range from 16 to 30 g/m² (143-268 lbs/acre) (WHO 1995). Doses used to control soil-borne fungi are typically higher than those used to control other pests, such as nematodes and insects. According to the United States Department of Agriculture (USDA), the United States uses about 5.98x10⁷ lbs (2.72x10⁷ kg) of methyl bromide annually (USDA 2004). Globally, about 16.76x10⁷ lbs (7.62x10⁷ kg) of methyl bromide was used in 1992 (Butler and Rodriguez 1996).

Approximately 75% of all methyl bromide produced is used to fumigate soil prior to planting crops, 11% is used to fumigate harvested commodities, 6% is applied to fumigate buildings such as food processing facilities and warehouses, and the remainder is used to produce other chemicals (USDA 2004). The majority of methyl bromide applications for agricultural activity are depicted in Figure 1. However, recent data suggest that tomatoes and strawberry growers are the highest users of methyl bromide in California and Florida (USGS 1998).

Methyl bromide is also emitted in small quantities from motor vehicle exhaust, but uncertainty in how much leaded gasoline is still used has made the estimated global emissions from this source difficult to quantify. This range has been reported to range anywhere from about 500,000 kg to 22,000,000 kg annually (Butler and Rodriguez 1996).

Recent estimates suggest that the stratospheric concentration of methyl bromide is approximately 8 to 9 parts per trillion (ppt) (WMO 2002). The lifetime of methyl bromide in the stratosphere has been estimated as about 35 years (Butler and Rodriguez 1996). The Montreal Protocol of 1991 classified methyl bromide as an ozone depleting substance and subsequent meetings called for the manufacture and importation of methyl bromide to be gradually phased out. Due to its importance as an agricultural fumigant, the U.S. Government has submitted "critical use exemptions" from the methyl bromide "phase-out" program. The U.S. nomination for a critical

METHYL_BROMIDE

ESTIMATED ANNUAL AGRICULTURAL USE

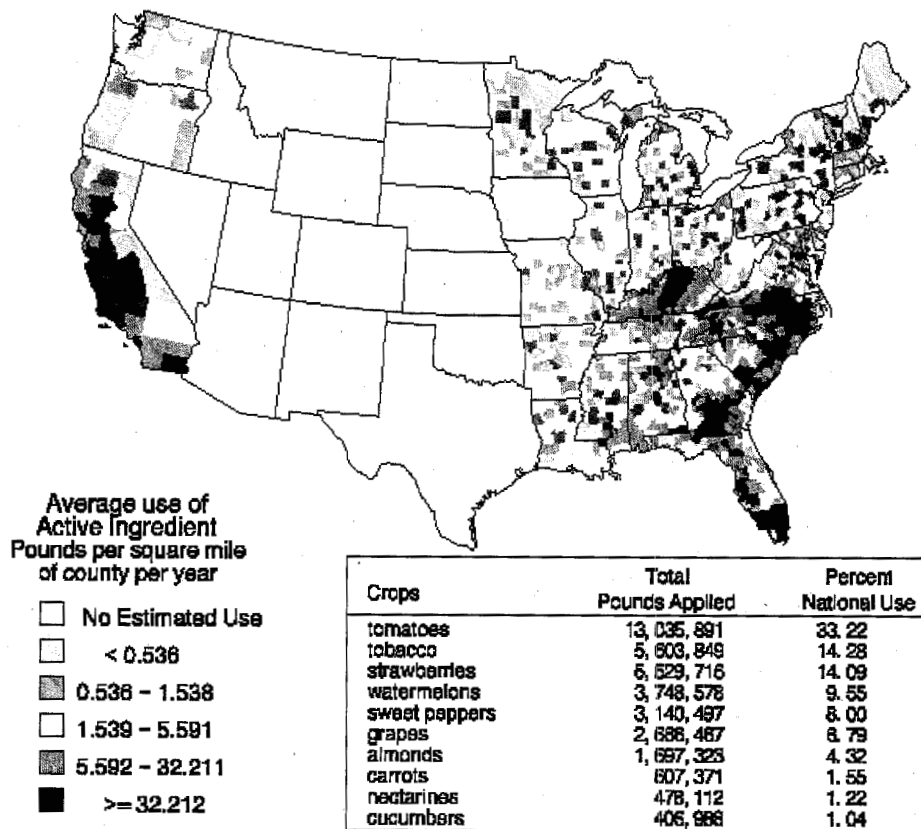


Figure 1. Map of methyl bromide use as pesticide in the United States. Pesticide Use National Synthesis Project (<http://ca.water.usgs.gov/pnsp/use92/mthlbrmid.html>). Map created by USGS. Pesticide use rates are based on data from the National Center for Food and Agricultural Policy. Data is collected from state and federal agencies and represents years 1990 - 1993 and 1995.

use exemption is for the following sixteen (16) crops/uses: commodity storage, cucurbit, eggplant, food processing, forest tree seedling nursery, ginger, nursery seed bed trays, orchard nursery, orchard replant, ornamental nursery, pepper, strawberry, strawberry nursery, sweet potato, tomato, and turfgrass. The total amount of methyl bromide nominated by the U.S. for these uses is 21,875,683 lbs (9,920,965 Kg) for 2005, and 20,827,018 lbs (9,445,360 Kg) for 2006. The proposed amounts for U.S. consumption of methyl bromide will decrease to 39% of the current usage for 2005, with a further decline in consumption to 37% in 2006. The detailed information supporting the U.S. nomination for CUE can be found in <http://www.epa.gov/spdpublic/mbr/cueqa.html>.

Recent data from the United Nations Environmental Programme (UNEP) Ozone Secretariat reported that global consumption of methyl bromide has been decreasing. The consumption of methyl bromide in 1999 was about 2.42×10^7 lbs (1.1×10^7 kg) less than 1998, suggesting compliance with the scheduled reductions was occurring (UNEP 2002).

III. INTEGRATED ENVIRONMENTAL RISK CHARACTERIZATION

Methyl bromide is a widely used fumigant on agricultural sites as a preplant soil sterilant to control nematodes, soil-borne diseases, insects and weeds. The high vapor pressure and low affinity for sorption on soil of methyl bromide suggest that volatilization is the most important environmental route of dissipation and to a lesser extent leaching and degradation. Methyl bromide is considered as an ozone depleting substance. Inhalation of methyl bromide vapor following soil fumigation is considered to be the major route of exposure for terrestrial organisms. An analysis using mammal inhalation data, estimated bird inhalation data, monitoring data, and model estimated edge-of-field air concentrations of methyl bromide does not appear to indicate a potential acute concern. Birds and mammals could have territories or home ranges in the area and be exposed continuously or repeatedly, due to the use of methyl bromide on multiple fields over multiple days in any given geographic area. Chronic inhalation toxicity data would be needed to address this potential exposure. The acute aquatic endangered species LOC is exceeded for aquatic invertebrates in two of the four modeled scenarios. Additional aquatic and terrestrial data are identified to provide a more comprehensive risk assessment and reduce uncertainties.

A. Environmental Fate

In soil and water, methyl bromide is degraded by a combination of abiotic (hydrolysis half-lives ≤ 15 days) and biotic (aerobic soil half-lives 6 to 57 days) processes, and the rate of these reactions influences the amount of methyl bromide that is ultimately volatilized to the atmosphere. In soils, the rate of degradation appears to be correlated to the amount of organic matter contained in the soil. Soils rich in organic matter have shown greater rates of degradation than soils low in organic matter. Soil moisture content, temperature, field management practices also significantly affect the relative amounts of methyl bromide volatilization following fumigation. Covering a field with a tarp immediately following fumigation has been shown to be an effective technique at increasing degradation and attenuating the amount of methyl bromide which is volatilized to the atmosphere. Methyl bromide released to the atmosphere is not only degraded through its reaction with photochemically produced hydroxyl radicals, but is also re-deposited back into oceans and soils which act as major sinks as well. The most recent estimates for the total lifetime of atmospheric methyl bromide is approximately 0.7 years, which leads to an ODP of about 0.38. These numbers are substantially lower than previous estimates. The greatest uncertainty in quantifying the total lifetime of methyl bromide in the environment remains quantifying all of its major release sources and the rate of degradation in air, water, and soil. In the atmosphere, the rate of degradation is highly dependent upon the concentration of photochemically produced hydroxyl radicals which varies spatially and temporally.

Background levels of methyl bromide range from about 10-26 ppt in the Northern hemisphere and about 9-15 ppt in the Southern Hemisphere. Agricultural areas where methyl bromide is used as a fumigant have concentrations that are several orders of magnitude greater than such typical background levels. Ambient air concentrations in agricultural areas where methyl bromide is frequently used are around 1 ppb, although levels in the ppm range are not uncommon at low altitudes immediately after a field has been fumigated.

The relatively low K_{oc} ($\leq 32.01 \text{ L Kg}^{-1}$) for methyl bromide suggests that this compound will not adsorb strongly to soils, possesses high mobility, and could ultimately leach into groundwater. However, the rapid volatilization and degradation rates of methyl bromide in soil will reduce the potential of this chemical to leach. The lack of detection of methyl bromide in groundwater strongly suggest that although methyl bromide is very mobile in soils, it is either volatilized or degraded before migrating to lower soil horizons and contaminating groundwater. Methyl bromide applied to a field has the potential to move into nearby surface waters through runoff and erosion. However, the Henry's Law Constant of $744 \text{ Pa-m}^3/\text{mol}$ suggests that it will be volatilized from surface water.

B. Ecological Risk

EFED's concern with methyl bromide is that it is highly volatile and can off-gas from treated fields and potentially expose a range of nontarget terrestrial organisms in its path. It also has the potential to reach surface water bodies through runoff under a possible worst-case scenario, that is, if an intense rainfall and/or continuous irrigation occurs right after application.

EFED used the screening-level $\text{LD}_{50}/\text{sq ft}$ method as a preliminary step to assess risks of the pesticide to birds and mammals. This method has most frequently been applied to pesticide application scenarios involving granular formulations, seed treatments, and baits. The method has not been generally applied to situations involving highly volatile compounds in the past, but remains the Agency's most appropriate index for this type of use, and was most recently used as part of a metam-sodium/MITC analysis. This $\text{LD}_{50}/\text{sq ft}$ method is an index that does not systematically account for exposures from each potential route, but considers the overall potential for adverse effects given a bioavailable amount of pesticide conservatively related to the mass applied per unit area at the treatment site. See the uncertainty discussion in Section VII.

Three mammal body weights are assessed: 15 g, 35 g, and 1000 g. The resulting risk quotients for these three sizes of mammals are 3,229, 1,384, and 48, respectively (see Section VII). These far exceed the acute risk LOC of 0.5, as well as the acute restricted use LOC of 0.2 and the acute endangered species LOC of 0.1. Using this same $\text{LD}_{50}/\text{sq ft}$ screen for birds, three avian weights are assessed: 10 g, 400 g, and 4000 g. The resulting risk quotients for these three sizes of birds are 5,705, 143, and 14, respectively. These far exceed the acute risk LOC of 0.5, as well as the acute restricted use LOC of 0.2 and the acute endangered species LOC of 0.1. Thus, these preliminary screens indicate a potential for concern for risk to wild mammals and birds, and the refined analyses based specifically on inhalation exposure for these animals are described below.

Owing to the limitations of the $LD_{50}/sq\ ft$ method for highly volatile compounds and the recognized high potential volatility of methyl bromide, EFED investigated the potential for inhalation to be a toxicologically significant route of exposure to birds and mammals within the use area. While data on inhalation toxicity are available for mammals (from HED), inhalation toxicity data are not available for birds. However, avian inhalation toxicity can be estimated where there are acute oral and inhalation data for mammals and acute oral data for birds.

A screening-level spreadsheet developed by EFED (Ed Odenkirchen, 12/16/03, OPP-EFED-USEPA) estimates avian inhalation toxicity and calculates mammalian and estimated avian risk quotients when there are known air concentrations and the above three toxicity values are available. The spreadsheet uses these values plus the molecular weight of the toxicant, bird weight, a mammal inhalation conversion factor, and a mammal to bird conversion factor to calculate the risk quotients. Specifically, the spreadsheet converts an air concentration to a dose, converts a mammal inhalation LC_{50} to an LD_{50} , and estimates an avian inhalation LD_{50} based on the three available toxicity values and a mammal to bird conversion factor. The avian risk quotient is the ratio of the dose to the estimated avian inhalation LD_{50} . The mammalian risk quotient is the ratio of the air concentration to the mammal inhalation LC_{50} (Appendix E, Tables E3 and E4).

Using the methyl bromide air concentration of 27 ppm from Table 6 (Bond and Dumas, 1987), mammal oral LD_{50} of 86 mg/kg, mammal inhalation LC_{50} of 3.03 mg/L (780 ppm), and avian acute oral LD_{50} of 73 mg/kg, a mammal acute inhalation risk quotient of 0.035 is calculated and an estimated avian acute inhalation risk quotient of 0.076 is calculated (Appendix E, Table E3).

Of course, monitoring data for one application site is not predictive of all site conditions where the pesticide may be used. Also, most monitoring data is for samples collected at least 0.5 m above the ground, often higher. This height is above the level for many ground-dwelling mammals and ground-feeding birds. It is reasonable to assume a gradient of concentrations at the treatment site, with higher concentrations of methyl bromide occurring closer to the ground. This would be primarily applicable to those reportedly few times that a tarp is not used (and animals would be more likely to be on the soil surface of the treated field). The ISCST model provides more flexibility compared to the monitoring data (i.e., results are more easily extrapolated) and generally allows the Agency to consider a much broader set of circumstances in its assessments. Nevertheless, since EFED is relying on HED data, the model calculation does not specifically produce on-field, ground surface level air residues. Because of uncertainties associated with each of the approaches, the Agency has calculated risk estimates based on both.

The ISCST model estimated methyl bromide concentrations were used in calculating the concentrations on the edge of the field from a field application of methyl bromide. The highest air concentration of 9.12 ppm (35.58 mg/m³) was estimated immediately adjacent to the field, with a 40-acre field, a 400 lb. ai/A application rate, and 0.80 emission ratio (Figure 2C). Using this input to the risk quotient spreadsheet with the same additional inputs as above, produces a

mammal acute inhalation risk quotient of 0.01 and an estimated avian acute inhalation risk quotient of 0.03 (Appendix E, Table E4).

The Agency has not established level of concern (LOC) thresholds expressly for the interpretation of RQs calculated for inhalation exposure risks. However, if the existing LOC criteria for acute bird and wild mammal risk were used to evaluate such RQs, the above analysis would suggest that neither mammal nor bird acute inhalation risk exceeds even the lowest of the LOCs (endangered species, 0.1). Given that most exposure is likely to be below the air exposure values used, often well below (see Table 6), this analysis does not appear to indicate an acute risk. Thus, based on this inhalation analysis, the initial potential for concern based on the preliminary LD₅₀/sq ft analysis has not been confirmed. However, there is some uncertainty in the inhalation analysis. The uncertainty level for birds in this inhalation analysis can be reduced by submission of avian inhalation toxicity data.

The above assessment is focused on acute effects and exposure windows. Wild mammals and birds may have home ranges or territories in the vicinity of the treatment area and may be exposed repeatedly as the result of methyl bromide use on multiple fields over multiple days in any geographic area, in addition to continued exposure from the methyl bromide off-gassing from any given field. Because of this potential for repeated and continued exposure, there may be a potential for chronic effects. The dog 5 -7 week inhalation LOAEL for methyl bromide is 5.3 ppm (NOAEL < 5.3 ppm), substantially lower than the mammal inhalation LC50 of 780 ppm. Nevertheless, 5.3 ppm is still well above even most of the peak air concentration values from Table 6. It is also well above the ambient air concentration data found in Table 4, where the highest values (not counting the reference regarding auto exhaust) are less than 1 ppb. Thus, it does not appear that methyl bromide would be likely to present a chronic risk to wild mammals. HED has indicated in their 1/6/03 HIARC report that a chronic mammal inhalation study (developmental neurotoxicity study) with methyl bromide is needed. Following HED review of this data, EFED may need to revise its comments on potential chronic risk to wild mammals. Chronic inhalation data are not available for birds, nor is EFED able to estimate chronic toxicity. A chronic avian inhalation study will enable EFED to address chronic exposure to birds.

Based on the labeled phytotoxicity of methyl bromide and multiple plant studies of various types that have been conducted, it is expected that non-target plants off-site may also be a risk from methyl bromide. Terrestrial plant guideline toxicity data are needed to evaluate this risk. LOCs for aquatic plants are not exceeded based on available data, but additional toxicity data are needed to complete this assessment.

EECs to determine the acute and chronic risk to aquatic organisms from methyl bromide were estimated using PRZM/EXAMS models with selected scenarios (tomatoes, strawberries, grapes, tobacco) to represent the numerous crops for which methyl bromide is registered for use. Based on this exposure assessment, California tomatoes (RQ, 0.06) and Florida strawberries (RQ, 0.07) exceed the acute endangered species LOC (0.05) for aquatic invertebrates. There is an uncertainty in estimating methyl bromide exposure due to post-application tarping of the treated

area and its relation to chemical loading through runoff in water bodies. Given the low levels of exceedence (RQs of 0.06 to 0.07), the potential effect of tarping might reduce the exposures, which in turn might reduce the RQs below the LOC.

Acute LOCs for freshwater fish are not exceeded, but the analysis is based on supplemental data. Chronic aquatic LOCs are not exceeded for freshwater fish, but the analysis is based on open literature data only. Core acute and chronic fish data on methyl bromide are needed to more fully evaluate risk to fish.

Monitoring data for the bromide ion (degradate of methyl bromide) includes several values above the available literature NOAEC for adverse effects on reproduction in both fish and aquatic invertebrates. However, bromide concentrations in the monitoring data are not associated with a soil fumigation of methyl bromide; thus, it is unclear how these concentrations would correspond to water contaminated with methyl bromide runoff from a nearby field or to exposures scenarios for aquatic receptors. Therefore, Tier I GENEEC model was used in estimating bromide ion EECs. The maximum chronic concentration for the modeled pond was slightly below the chronic endpoints based on open literature data. Guideline chronic ecological effects data on the bromide ion are needed for a complete assessment and to reduce uncertainty.

The focus of the present review is on the direct toxicity of methyl bromide and the bromide ion degradate, and the risks they pose to plants and animals. There are also potential indirect effects resulting from the effect of methyl bromide on atmospheric ozone levels. Reductions in stratospheric ozone levels due to ozone-depleting chemicals such as methyl bromide can lead to increased levels of solar ultraviolet radiation (UVB) reaching the earth. This, in turn, can have both direct and indirect effects on plants and animals. EPA and other federal agencies continue to investigate these potential effects. For example, solar UVB radiation can result in reduced survival and production in phytoplankton, the foundation of aquatic food webs. It can also damage early developmental stages of amphibians, fish, shrimp, and crabs, for example (USEPA web page: <http://www.epa.gov/ozone/science/effects.html>).

C. Endangered Species

The Agency's Levels of Concern (LOC) for endangered and threatened aquatic invertebrates are exceeded for two of four modeled use patterns, based on methyl bromide concentrations. A similar ratio may also apply to the many additional, non-modeled use sites. The preliminary analysis indicates that there is unlikely to be a potential acute risk to endangered birds and mammals from inhalation, based on available monitoring and modeling data. Further data are needed to refine this analysis. It is expected that any insects or other terrestrial invertebrates exposed to methyl bromide would be adversely affected. At present, methyl bromide is labeled widely for virtually all crops. If the registrants can narrow the labels to specific crops, a list of endangered/threatened species associated with these specific crops can be provided. Although endangered species LOCs are exceeded using freshwater invertebrate data,

the oyster (marine/estuarine) is very likely to be more representative of endangered/threatened freshwater molluscs than is the freshwater daphnid. This is a data gap for methyl bromide.

The Agency has developed the Endangered Species Protection Program to identify pesticides whose use may cause adverse impacts on endangered and threatened species, and to implement mitigation measures that address these impacts. The Endangered Species Act requires federal agencies to ensure that their actions are not likely to jeopardize listed species or adversely modify designated critical habitat. To analyze the potential of registered pesticide uses to affect any particular species, EPA puts basic toxicity and exposure data developed for REDs into context for individual listed species and their locations by evaluating important ecological parameters, pesticide use information, the geographic relationship between specific pesticide uses and species locations, and biological requirements and behavioral aspects of the particular species. This analysis will take into consideration any regulatory changes recommended in this RED that are being implemented at this time. A determination that there is a likelihood of potential impact to a listed species may result in limitations on use of the pesticide, other measures to mitigate any potential impact, or consultations with the Fish and Wildlife Service and/or the National Marine Fisheries Service as necessary.

As part of the interim program, the Agency has developed County Specific Pamphlets that articulate many of the specific measures outlined in the Biological Opinions issued to date. The Pamphlets are available for voluntary use by pesticide applicators on EPA's website at www.epa.gov/espp. A final Endangered Species Protection Program, which may be altered from the interim program, was proposed for public comment in the Federal Register December 2, 2002.

D. Endocrine Disruption

Methyl bromide does not appear to present a specific endocrine disruption risk at present. Nevertheless, EPA is required under the FFDCA, as amended by FQPA, to develop a screening program to determine whether certain substances (including all pesticide active and other ingredients) *"may have an effect in humans that is similar to an effect produced by a naturally occurring estrogen, or other such endocrine effects as the Administrator may designate."* Following the recommendations of its Endocrine Disruptor Screening and Testing Advisory Committee (EDSTAC), EPA determined that there was a scientific basis for including, as part of the program, the androgen and thyroid hormone systems, in addition to the estrogen hormone system. EPA also adopted EDSTAC's recommendation that the Program include evaluations of potential effects in wildlife. For pesticide chemicals, EPA will use FIFRA authority, and, to the extent that effects in wildlife may help determine whether a substance may have an effect in humans, FFDCA authority, to require the wildlife evaluations. As the science develops and resources allow, screening of additional hormone systems may be added to the Endocrine Disruptor Screening Program (EDSP). When the appropriate screening and/or testing protocols being considered under the Agency's EDSP have been developed, methyl bromide may be

subjected to additional screening and/or testing to better characterize effects related to endocrine disruption.

IV. ENVIRONMENTAL FATE AND TRANSPORT CHARACTERIZATION

(A) Physical, Chemical, and Environmental Fate Properties of Methyl Bromide

Methyl bromide is colorless gas at ambient temperature and pressure with a boiling point of 4.5°C. It is highly soluble and has high vapor pressure. Based on the Henry's law constant, volatilization from soil and water surfaces is expected to be an important fate process. Once it volatilized, methyl bromide degrades in the upper atmosphere through its reaction with hydroxyl radical, the estimated lifetime in air is 303 days. The pertinent physical, chemical, and environmental fate properties relating to methyl bromide are illustrated in Table 1.

Table 1. Physical, chemical, and Environmental Fate Properties of methyl bromide.

Parameters	Values and Units	Sources
Chemical Name: Bromomethane		
Common Name: Methyl Bromide		
Chemical Class: Alkyl bromide		
Chemical Abstract Number: 74-83-9		
Physical and Chemical Properties		
Molecular Formula	CH ₃ Br	Tomlin 1994
Molecular Weight	94.94	Tomlin 1994
Color	Colorless	Tomlin 1994
Odor	Odorless at room temperature. Chloroform-like odor at high concentrations.	Tomlin 1994
Physical State	Gas	Tomlin 1994
Melting Point	-93 °C	Tomlin 1994
Boiling Point	4.5 °C	Tomlin 1994
Water Solubility	15.2 g/L at 25 °C	Horvath 1982
Log K _{ow}	1.19	Hansch et al. 1995
Vapor Pressure	216 kPa at 25 °C	Dauber and Danner 1989
Henry's Law Constant	744 Pa-m ³ /mol	Yates and Gan 1998
Density	1.6755 g/cm ³	Lide 1998
Ozone Depletion Potential (ODP)	0.38	World Meteorologic Organization (WMO) 2002

Table 1. Physical, chemical, and Environmental Fate Properties of methyl bromide.

Parameters	Values and Units	Sources
Environmental Fate Properties		
Hydrolysis Half-Lives @ 25°C in distilled water	11 days (pH = 5) 11 days (pH = 7) 15 days (pH = 9)	MRID 42720201
Atmospheric lifetime	303 days (assumes a constant hydroxyl radical concentration of 1×10^6 molecules/cm ³)	Atkinson 1989
Photodegradation in Half-Lives @ 25°C in distilled water	9 days	MRID 4272301
Degradation Half-Lives in Soil (aerobic)	Bi-phasic half-lives 1 st half-life: 1.5 days (Sandy loam) 2 nd half-life: 20 days (Sandy loam) 1 st half-life: 0.15 days (Clay loam) 2 nd half-life: 19 days (Clay loam)	MRID 40863301
	38.5 days (Sandy loam; 0.92% OM) 3.6 days (Clay loam; 2.51 % OM)	Papiernik et al., 2000
	22 days (Sandy loam; 0.92% OM) 6 days (Loamy sand; 2.51 % OM) 6 days (Clay loam; 2.99 % OM) 6 days (Nursery potting mix; 9.6 % OM)	Gan and Yates, 1996
	27.1 days (moist sandy loam; 0.92% OM) 33.5 days (moist sandy loam; 0.65%OM) 57.3 days (moist loamy sand; 0.22%OM) 11.4 days (moist clay loam; 2.99% OM)	Gan et al. 1994
	12.6 days (air-dried sandy loam; 0.92%OM) 24.1 days (air-dried sandy loam; 0.65%OM) 38.7 days (air-dried loamy sand; 0.22%OM) 5.8 days (air-dried clay loam; 2.99% OM)	
	35.9 days (oven-dried sandy loam; 0.92% OM) 59.2 days (oven-dried sandy loam; 0.65%OM) 26.8 days (oven-dried loamy sand; 0.22%OM) 46.8 days (oven-dried clay loam; 2.99% OM)	

Table 1. Physical, chemical, and Environmental Fate Properties of methyl bromide.

Parameters	Values and Units	Sources
Degradation Half-Life in Soil (anaerobic)	Bi-phasic half-life 1 st half-life: 6.0 days (Sandy loam, 2 nd half-life: 24 days ((Sandy loam) 1 st half-life: 1.6 days (Clay loam 2 nd half-life: 20 days (Clay loam)	MRID 40863301
Degradation Half-Life in Water	5 days (freshwater) 36 days (estuary water) 82 days (coastal seawater) 298 days (hypersaline water samples)	Goodwin et al. 1998
Soil Water Partition Coefficient (K_{oc})	7.07 L Kg ⁻¹ for loamy sand soil 32.01 L Kg ⁻¹ for loamy sand soil 17.40 L Kg ⁻¹ for loam soil 16.38 L Kg ⁻¹ for Peaty clay soil	Daelemans and Siebering (1977)

(B) TRANSPORT AND PARTITIONING

(i) Volatilization

The high vapor pressure and Henry's Law constant indicate that volatilization of methyl bromide from soil and water surfaces occurs rapidly. Anderson et al. (1997) studied the volatilization properties of methyl bromide applied as a liquid to the surface of a sandy clay loam (53% sand, 29% silt, 17% clay, 3.1% organic matter, pH = 6.6) as a function of temperature and moisture content. The results of this study indicated that volatilization of methyl bromide from the soil surface increased with increasing temperature and moisture content. At a moisture content of 0.3 bar, 32.2%, 35.2% and 54.4% of the applied methyl bromide was lost to volatilization in 119 hours at 15, 25, and 35 °C, respectively. At a constant incubation temperature of 25 °C, 4.1%, 28.9% 34.7%, and 66.7% was volatilized within 72 hours at a moisture content of 3, 1, 0.3, and 0.03 bar, respectively (Anderson et al. 1997). Gan et al. (1996, 1997) also observed rapid volatilization of methyl bromide from treated soils, but concluded that volatilization occurred more rapidly in dry soils as compared to moist soils when methyl bromide was injected as a gas into the subsurface soil. Forty milliliters of methyl bromide gas was injected at a depth of 30 cm into packed columns containing either Greenfield sandy loam (9.5% clay, 0.92% organic matter, pH = 7.4), Carsitas loamy sand (0.1% clay, 0.22% organic matter, pH = 7.2), or a Linne clay loam (25.1% clay, 2.99% organic matter, pH = 8.0). Volatilization was almost instantaneous from the Greenfield sandy loam and Carsitas loamy sand, with a maximum volatilization rate of 9.7-15.8 mg/hour achieved within 2.5 hours. The cumulative volatilization losses from the Greenfield and Carsitas soils were about 90% (Gan et al. 1996). However, with the Linne clay loam under the same conditions, only about 44% of the applied methyl bromide was volatilized. The large difference in volatilization was primarily attributed to the rapid rate of degradation which occurred in the richly organic Linne clay loam (Gan et al. 1996). Analysis of the soils

following the experiments concluded that approximately 49% of the applied methyl bromide had been degraded in the Linne clay loam, while only about 10% degradation occurred in the other 2 soils. It was also observed that increasing the volumetric water content of the Greenfield sandy loam from $0.058 \text{ cm}^3/\text{cm}^3$ to $0.180 \text{ cm}^3/\text{cm}^3$ resulted in a decrease in volatilization of methyl bromide (Gan et al. 1996). It was reasoned that as the moisture content increased, the effective gas phase diffusion coefficient of methyl bromide in the soil decreased resulting in a lower surface volatilization flux and a greater amount of degradation (Gan et al. 1996, 1997).

Similar experiments were conducted using methyl bromide and methyl iodide in which the soil columns were covered with a high density polyethylene (HDPE) tarp, high barrier plastic tarp, or left completely uncovered (Gan and Yates 1996; Gan et al. 1997). In each experiment it was noted that greater volatilization losses were observed in soils that were left uncovered and contained the lowest amounts of organic matter. It was also observed that under similar conditions a greater percentage of methyl iodide was volatilized as compared to methyl bromide due to the relatively slow rate of degradation of methyl iodide (Gan and Yates 1996; Gan et al. 1997). Covering the soils with a tarp following fumigation was shown to be an effective method of attenuating the rate of volatilization. Using a Greenfield sandy loam with approximately 0.92% organic matter, the cumulative volatilization loss of methyl bromide injected at a depth of 60 cm was 75%, 68%, and 45% for an uncovered soil column, a soil column covered with HDPE, and a soil column covered with a high barrier plastic film (Gan et al. 1997). Packed soil column experiments using an Arlington sandy loam (0.92% organic matter, pH = 7.2) indicated that approximately 88% of the injected methyl bromide was volatilized if the soil surface was left uncovered (Gan et al. 2000). Volatilization losses were 83%, and 55% of the nominal methyl bromide concentration when the soil columns were covered with a HDPE tarp, and a high barrier plastic tarp, respectively (Gan et al. 2000). The addition of soil amendments rich in organic matter were also shown to be an effective method of reducing volatilization losses of methyl bromide by enhancing the rate of degradation (Gan et al. 1998). Applying 5% composted manure to soil columns containing methyl bromide reduced volatilization approximately 12% as compared to unamended soil columns (Gan et al. 1998).

Field experiments conducted in Monterey County, California have also demonstrated the effectiveness of covering the treated area following the application of methyl bromide in order to attenuate volatilization (Majewski et al. 1995). A fumigant composed of methyl bromide/chloropicrin was injected at a depth of 25-30 cm in liquid form at an application rate of 392 kg/ha to fields located approximately 6 km away from each other. One field was immediately covered with a high barrier plastic tarp while the other field was left uncovered. Both fields were a silty clay loam with similar soil texture, moisture content, and organic matter composition. The cumulative volatilization loss of methyl bromide from the tarpaulin covered field was about 22% five days post-application and about 32% nine days post-application. In contrast, the cumulative volatilization loss of methyl bromide from the uncovered field was about 89% by the fifth day (Majewski et al. 1995). The maximum volatilization flux of methyl bromide from the covered field occurred about 24-36 hours post-application and was approximately $100 \mu\text{g}/\text{m}^2\text{-sec}$, while the maximum volatilization flux from the uncovered field

was about 4 times greater and occurred earlier in the experiment. Wang et al. (1997) also demonstrated that field management practices can significantly reduce the volatilization of methyl bromide from treated fields. Methyl bromide was injected at concentrations of about 600-700 grams per plot into an Arlington fine sandy loam (64% sand, 29% silt, 7% clay) near Riverside, California. At an injection depth of 25 cm the total volatilization losses were 87%, <42%, and 59% for uncovered plots, plots that were immediately irrigated and covered by a HDPE tarp, and non irrigated plots covered by HDPE tarpaulins, respectively. At an injection depth of 60 cm the volatilization losses were 60%, 15% and <15% for uncovered plots, HDPE covered plots, and plots covered by a high barrier plastic tarpaulin, respectively.

At application rates of 300-800 lbs/acre, methyl bromide injected at a depth of 1 foot, dissipated with a half-life of less than 4 days in field plots located in California (MRID 00013032). The concentration of methyl bromide at depths greater than the injection point generally increased until 6-8 days post-application when tarpaulins covering the fields were removed. Similar results were observed when methyl bromide was injected at a depth of 1 foot at application rates of 136.2-363.2 kg/ha (MRID 00013173). Field dissipation half-lives of less than 3 to less than 7 days were observed and the levels of methyl bromide at deeper depths generally increased until the HDPE tarpaulins were removed.

The volatilization kinetics of methyl bromide in water have also been studied under controlled laboratory conditions. Methyl bromide solutions at 50, 150 and 300 μM concentrations were placed in a beaker containing 400 ml of distilled water and gently stirred at 20°C (Gentile et al. 1989). In all cases volatilization occurred rapidly, with volatilization half-lives on the order of a few hours or less.

(ii) Adsorption

USDA reports K_{oc} values of methyl bromide in the range of 9-22, but no experimental details were provided (USDA 2004). Daelemans and Siebering (1977), measured soil adsorption isotherms of methyl bromide in a loamy sand, a loam, and a peaty clay at different moisture contents. The K_{om} (soil adsorption coefficient normalized with organic matter) ranged from 4.10-18.37 in the loamy sand and was 10.09 and 9.50 in the loam and peaty clay, respectively. Using the relationship $K_{oc} \sim 1.724 \times K_{om}$ (Lyman et al. 1990), these correspond to K_{oc} values of approximately 7-32.

Adsorption and desorption of methyl bromide was studied in water with respect to four different soil types and several different methyl bromide concentrations (MRID 00157128). The amount of methyl bromide adsorbed to the soils increased with increasing methyl bromide content in water and the adsorption was reversible. It was observed that 89-97% desorption of methyl bromide adsorbed to the surface of the soils was achieved with a single washing.

The relatively low K_{oc} for methyl bromide suggests that this compound will not adsorb strongly to soils, possesses high mobility, and could ultimately leach into groundwater. However, the rapid volatilization and degradation rates of methyl bromide in soil will reduce the potential of

this chemical to leach. The lack of detection of methyl bromide in groundwater (see Section F - water monitoring data) strongly suggest that although methyl bromide is very mobile in soils, it is either volatilized or degraded before migrating to lower soil horizons and contaminating groundwater.

The adsorption of methyl bromide to plastic films and tarpaulins commonly employed to cover agricultural fields following application has been studied (Papiernik et al. 1999). Following injection of methyl bromide into airtight vials containing high density polyethylene (HDPE), Hytibar plastic film, and an experimental film from DowElanco, adsorption and desorption kinetics showed that methyl bromide adsorption to the surface of these films is linear and reversible. The least amount of adsorption was observed for the HDPE film, with approximately 7-18% of the injected amount adsorbed to the surface of the film. Sorption to the Hytibar and the Dow film was significantly greater, resulting in about 2-3 times more adsorption.

(C) PERSISTENCE

(i) Degradation in Air

Methyl bromide is degraded in the troposphere through its reaction with photochemically produced hydroxyl radicals. Direct photolysis, hydrolysis in water droplets, and degradation by other atmospheric oxidants such as nitrate radicals and ozone are not expected to be significant degradation pathways for methyl bromide in the atmosphere (Butler and Rodriguez 1996). Some methyl bromide may also migrate to the troposphere where it is degraded by UV light with an estimated lifetime of about 35 years (Butler and Rodriguez 1996). The vapor phase hydroxyl radical rate constant of methyl bromide has been measured as 3.81×10^{-14} cm³/molec-sec at 25 °C (Atkinson 1989), which corresponds to an atmospheric half-life of about 210 days assuming a hydroxyl radical concentration of 1×10^6 molec/cm³. The concentration of hydroxyl radicals in the atmosphere is not constant however, and is a function of solar irradiation, latitude, altitude, temperature, and the concentration of other atmospheric constituents. While it is difficult to directly measure the hydroxyl radical concentration, its global average has been estimated from the observed concentration and seasonal variation of methyl chloroform.

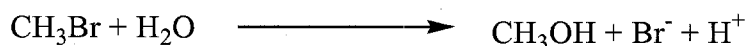
Since methyl chloroform is an anthropogenic substance that is removed from the atmosphere solely by reaction with the hydroxyl radicals and its emissions to the atmosphere are well characterized, a detailed profile of its concentration over time gives an indirect measure of the hydroxyl radical concentration. The atmospheric concentration of methyl chloroform has been measured daily since 1978 at five stations in the Atmospheric Lifetime Experiment Global Atmospheric Gasses Experiment (ALE/GAGE) network. These data were used to estimate the temporal global average hydroxyl radical concentration, as well as its temporal concentration in the Northern and Southern hemispheres (Prinn et al. 2001). A figure summarizing this data is reproduced in the Appendix B (Figure B1). An analysis of the data has shown that the hydroxyl radical concentration in the atmosphere had increased from 1978 to 1988, but has been decreasing slightly ever since (Prinn et al. 2001). Current estimates of the average hydroxyl radical concentration are $8.98 \pm 2.02 \times 10^5$ molec/cm³ in the Northern Hemisphere and 9.93 ± 2.02

$\times 10^5$ molec/cm³ in the Southern Hemisphere (Prinn et al. 2001). Probability distribution (or density) functions (PDF) which represent the hydroxyl radical concentration globally and in both the Northern and Southern hemisphere were developed by Prinn et al. (2001). These distributions were used along with the hydroxyl radical rate constant given above to calculate the PDF and cumulative distribution function (CDF) for the atmospheric half-life of methyl bromide in the Northern and Southern hemisphere (Figures B2 and B3).

Figures B2 and B3 represent the PDF and CDF atmospheric oxidation half-life of methyl bromide assuming a constant hydroxyl radical rate constant. In reality, this rate constant is a function of temperature, and it may also vary slightly depending on geophysical location. Sophisticated multi-dimensional box models that take into account the variability in hydroxyl radical concentration and the temperature dependence of the rate constant have been developed by dividing the atmosphere into several different lower atmospheric and upper atmospheric boxes of varying temperature and hydroxyl radical concentration along the Northern and Southern hemisphere. These models have been developed to estimate the atmospheric lifetime of methyl chloroform (Miller et al. 1998; Prinn et al. 1995) and methyl bromide (Reeves and Penkett 1993). The global estimate for the lifetime of atmospheric methyl bromide using a two-dimensional box model was calculated as 1.78 years (Reeves and Penkett 1993).

(ii) Degradation in Water

The degradation of methyl bromide in soil and water occurs through a combination of abiotic processes and biodegradation. Butler and Rodriguez (1996) estimate that approximately 60-75% of the methyl bromide produced naturally in the world's oceans are degraded *in situ* by these reactions, and only about 25-40% are volatilized to the atmosphere. The hydrolysis of methyl bromide occurs through a S_N2 nucleophilic substitution reaction, resulting in the formation of methanol and the bromide anion.



Under neutral conditions and at a temperature of 25 °C, the half-life of methyl bromide in non-sterile purified deionized water was reported as 20 days (Papiernik et al. 2000). The hydrolysis half-life of methyl bromide was measured in distilled water at pH range 3-8, and at temperatures of 18 and 30 °C (Gentile et al. 1989). At a constant temperature of 18 °C the hydrolysis half-life of methyl bromide was reported as 29, 19, 12, and 9 days at pH 3, 5, 7, and 8, respectively. At an incubation temperature of 30 °C, the half-lives were 28, 18, 10, and 8 days at pH 3, 5, 7, and 8, respectively in the distilled water. The authors observed slightly longer hydrolysis half-lives in groundwater (pH range 7.5-7.8) obtained from Liguria, Italy. Half-lives in the range of 36-50 days were observed at a temperature of 18 °C, and half-lives of 15-19 days were reported in the well water at 30 °C (Gentile et al. 1989). Although the authors were unable to identify the precise reason for the difference in degradation rates between the distilled water and natural well water, they surmised that the reaction rate was affected by ionic species or adsorption to organics commonly found in the well water. In another study involving the hydrolysis of methyl bromide, the hydrolysis half-lives in water were given as approximately 11 days at pH 5 and 7, and 15 days

at pH 9 at 25 °C (MRID 42720201). Methanol and the bromide ion were detected in tests solutions at maximum concentrations of 16 and 58 ppm, respectively, after 30 days. These data are summarized in Table 2.

Table 2. Hydrolysis half-life of methyl bromide.

Temperature (°C)	pH	Half-Life (days)	Reference
25	7	20	Papiernik et al. 2000
18	3	29	Gentile et al. 1989
18	5	19	Gentile et al. 1989
18	7	12	Gentile et al. 1989
18	8	9	Gentile et al. 1989
30	3	28	Gentile et al. 1989
30	5	18	Gentile et al. 1989
30	7	10	Gentile et al. 1989
30	8	8	Gentile et al. 1989
25	5	11	MRID 42720201
25	7	11	MRID 42720201
25	9	15	MRID 42720201

Gentile et al. (1989) noted that the rate of hydrolysis was enhanced upon exposure to UV irradiation. Similar observations were noted by Castro and Belser (1981) who observed a 6 to 7 fold increase in the hydrolysis rate of methyl bromide in aqueous solution at neutral conditions when irradiated with UV light at 254 nm (MRID 00147719). The enhanced degradation was attributed to hydrolysis of an excited state of methyl bromide, but since this compound has only weak absorption above 290 nm, it is doubtful that this enhanced hydrolysis rate is of environmental significance. The half-life of aqueous solutions of methyl bromide at 25 °C was approximately 9 days at pH 5 and 7, and 15 days at pH 9 when irradiated with light from an artificial light source (MRID 42720301). The half-lives were approximately 11 days (pH 5 and 7) and 15 days (pH 9) in dark controls; suggesting that hydrolysis, not photolysis is the primary degradation mechanism. The degradation products in both the irradiated samples and dark controls were methanol and the bromide ion. Maximum concentrations of both were reached after 30 days, with methanol ranging from 18-21 ppm, and bromide ion at 88, 66, and 38 ppm in the pH 5,7, and 9 solutions, respectively.

The hydrolysis of methyl bromide was studied at pH 5,7, and 9, at temperatures of 25 and 35 °C (MRID 00147718). Degradation rates of 1.2 to 1.5 mg methyl bromide/L/day were observed at

25 °C at each pH; but the hydrolysis rates were reported to be about 4-5 times higher at 35 °C (MRID 00147718).

The bacterial oxidation of methyl bromide in freshwater, estuary water, coastal seawater, and hypersaline-alkaline water was studied by monitoring the production of $^{14}\text{CO}_2$ produced from samples of $^{14}\text{CH}_3\text{Br}$ incubated in the water samples (Goodwin et al. 1998). The half-lives were approximately 5, 36, 82, and 298 days for the freshwater, estuary water, coastal seawater, and hypersaline-alkaline water samples, respectively (Goodwin et al. 1998). No $^{14}\text{CO}_2$ production was observed for sterilized controls. This data suggests that biotic degradation processes will occur at a rate similar to the hydrolysis rate in freshwater, but will be slower than the rate of hydrolysis in seawater.

(iii) Degradation in Soil

It has been suggested that methyl bromide reacts with nucleophilic sites found in soil organic matter resulting in the methylation of the organic matter and the release of the bromide anion (Papiernik et al. 2000). This reaction is abiotic in nature as was demonstrated by following the degradation kinetics of methyl bromide in an Arlington sandy loam (74.6% sand, 18.0% silt, 7.4% clay, 9.2 g/kg organic carbon, pH = 6.73) and a Linne clay loam (36.7% sand, 32.0% silt, 31.3% clay, 25.1 g/kg organic carbon, pH = 6.80) under sterile and non sterile conditions (Papiernik et al. 2000). The half-life of methyl bromide in the Arlington sandy loam was approximately 38.5 and 46.2 days in non autoclaved and autoclaved samples. The half-lives were about 3.6 and 4.2 days in non autoclaved and autoclaved Linne clay loam samples. Since the degradation rates were not significantly different in the autoclaved versus the non autoclaved soil experiments, the authors concluded that abiotic processes were largely responsible for the observed degradation. The greater content of organic matter in the Linne clay loam also resulted in much greater degradation rates than in the lower organic containing Arlington sandy loam. This observation is supported by the data of Gan and Yates (1996) that observed a similar correlation between the degradation rate of methyl bromide and soil organic matter content. In 4 soils containing 0.92%, 2.51%, 2.99%, and 9.60% organic matter, the half-life of methyl bromide was reported as 22, 6, 6, and 6 days, respectively and there was no statistically significant difference in degradation rates in sterilized versus non sterilized soils (Gan and Yates 1996). Similar trends in the degradation rate of methyl bromide were observed in studies using a Kimberlina sandy loam (63.1% sand, 13% silt, and 11.9% clay) and a Panoche clay loam (43.1% sand, 17% silt, and 39.9% clay) under aerobic and anaerobic conditions (MRID 40863301). In these experiments methyl bromide degradation was observed to be bi-phasic with an initial half-life of 35 hours and 47 hours in non sterilized and sterilized sandy loams, respectively while under aerobic conditions. The second half-lives were reported as 20 and 18 days in non sterilized and sterilized sandy loams, respectively under aerobic conditions. Under anaerobic conditions the average initial half-life was 144 hours for the non sterilized sandy loam and 80 hours for the sterilized loam. The second half-lives under anaerobic conditions were given as 24 days for the unsterilized sandy loam and 21 days for the sterilized loam. Under aerobic conditions the initial half-life of methyl bromide in the clay was 3.8 hours and 2.5 hours in non sterilized and sterilized clay loams respectively. The second half-lives were 19 and 11 days in

non sterilized and sterilized clays, respectively. In the anaerobic studies, the initial methyl bromide half-life was 39 and 34 hours for the unsterilized and sterilized clay loams. The second half-lives were reported as 20 days for the unsterilized clay loam and 18 days for the sterilized clay loam (MRID 40863301).

The degradation of methyl bromide in 4 California surface soils, a Greenfield sandy loam (9.5% clay, 0.921% organic matter, pH 7.39), Wasco sandy loam (4.3% clay, 0.646% organic matter, pH 6.98), Linne clay loam (25.1% clay, 2.989% organic matter, pH 7.23) and Carsetas loamy sand (0.1% clay, 0.222% organic matter, pH 8.02) was studied under moist, air dried, and oven dried conditions (Gan et al. 1994). Correlation analysis between the degradation rate constant and the properties of the soil indicated that the degradation of methyl bromide is highly correlated with the amount of organic matter contained in moist and air dried soils, but not oven dried soils. The regression derived equations provided by the authors were:

$$k_{\text{air-dried}} = 0.0090 + 0.0174(\%OM)$$

$$k_{\text{moist}} = 0.0116 + 0.0364(\%OM)$$

Each k represents the first-order degradation rate constant in terms of days⁻¹, and %OM reflects the percentage of organic matter contained in the soil. Half-lives of approximately 11 to 33 days and 6 to 39 days were calculated for the 4 soils under moist and air dried conditions (Table 1), while half-lives of roughly 27 to 59 days were estimated in the oven-dried soil experiments.

The microbial degradation of methyl bromide was shown to be enhanced significantly under aerobic conditions in methanotrophic soils (soils containing bacteria that readily oxidize methane) (Ou 1998). Using methanotrophic soils and an application rate of 1,000 µg/g, methyl bromide was completely degraded within 40-90 hours under aerobic conditions. At a lower application rate of 10 µg/g, methyl bromide was completely degraded in 5 hours under aerobic conditions, but degraded very slowly under anaerobic conditions (Ou 1998). The primary degradation products of methyl bromide from methanotrophic microbes has been reported as formaldehyde and the bromide anion (Ou 1998). While pointing out these results, the authors also noted that the majority of agricultural soils in the U.S. are not methanotrophic and have low methane oxidizing capabilities. Very low levels of methyl bromide were shown to be rapidly degraded by an agricultural (corn field) soil and highly organic forest soil obtained from southern New Hampshire under aerobic conditions (Hines et al. 1998). At concentrations of approximately 10 parts per billion (ppb) methyl bromide was completely degraded in the forest soil in a matter of minutes, and was completely degraded in the agricultural soil in a matter of hours. Almost no degradation occurred in autoclaved soils or soils that had previously been sterilized by the addition of antibiotics twelve hours earlier confirming that the source of degradation was biological. The authors reported that experiments using high levels of methyl bromide (10 to 10,000 ppm) resulted in toxicity to the microbes and slow degradation rates. Experiments conducted under a nitrogen rich environment showed little degradation of methyl bromide for any of the soils tested, suggesting that biodegradation is very slow under anaerobic

conditions. Although biodegradation under anaerobic conditions is considered to occur slowly in the environment, Oremland et al. (1994) demonstrated that methyl bromide may react with free sulfide commonly found in anaerobic sediments and salt marshes resulting in the production of methylated sulfur reaction products, which in turn are degraded by sulfate reducing bacteria.

(iv) Lifetime of Methyl Bromide

Estimating the total lifetime of methyl bromide is more difficult than estimating the lifetime of chlorofluorocarbons (CFC) because there are several sources of methyl bromide in the environment which are difficult to quantify, its emissions arise from both anthropogenic and natural origins, and there are several sinks for methyl bromide (See Appendix B). Difficulty in quantifying the precise emission rates and environmental sinks of methyl bromide result in a large degree of uncertainty in the estimated lifetime. Previous estimates of the lifetime of methyl bromide that considered only the photochemical sink (degradation by hydroxyl radicals and stratospheric photolysis) resulted in an atmospheric lifetime of about 1.7-1.8 years and an ozone depletion potential (ODP) of about 0.65 (Mellouki 1992). Recent data has suggested that soil surfaces and the oceans should also be considered major sinks for methyl bromide. The total lifetime of atmospheric methyl bromide can be determined from the sum of the reciprocal lifetime due to each major sink (Butler and Rodriguez 1996; Shorter et al. 1995; Yvon and Butler 1996):

$$\frac{1}{\tau_{total}} = \frac{1}{\tau_p} + \frac{1}{\tau_o} + \frac{1}{\tau_s} \quad (1)$$

where τ_{total} is the total lifetime of atmospheric methyl bromide, τ_p is the lifetime due to degradation via hydroxyl radicals and stratospheric photolysis, τ_o is the lifetime due to ocean uptake, and τ_s represents the lifetime due to soil uptake. Using lifetimes of 1.7, 2.7, and 3.4 years for τ_p , τ_o , and τ_s , the total atmospheric lifetime of methyl bromide (τ_{total}) was estimated as 0.8 years (Shorter et al. 1995; Yvon and Butler 1996). The total lifetime of methyl bromide has been derived based on the release of methyl bromide into the atmosphere, and does not include that portion of methyl bromide which has been degraded in the soil. The most recent WMO document on ozone depletion uses a best estimate of 1.9 years for τ_o , resulting in a total lifetime (τ_{total}) of 0.7 years (WMO 2002). The WMO cautions that the sources and sinks of methyl bromide are not thoroughly understood (WMO 2002). Therefore, this lifetime can only be considered a best estimate for the global lifetime of atmospheric methyl bromide.

(D) OZONE DEPLETION POTENTIAL

The ozone depletion potential (ODP) of a substance can be described by the ratio of the impact on the ozone layer of that substance compared to the impact of trichlorofluoro methane (CFC-11). Mathematically, ODP is calculated with the following equation (WMO 2002):

$$ODP(x) = FRF \cdot \alpha \cdot \frac{\tau_x}{\tau_{CFC-11}} \cdot \frac{M_{CFC-11}}{M_x} \cdot \frac{n_x}{3} \quad (2)$$

where *FRF* is the fractional release factor and describes the availability or release of a halogen from substance *x* with respect to CFC-11, α is the relative effectiveness of any halogen compared to chlorine for ozone destruction, τ_x is the lifetime of chemical *x*, τ_{CFC-11} is the lifetime of CFC-11, M_{CFC-11} and M_x are the molecular weights of CFC-11 and chemical *x*, respectively and n_x is the number of halogen atoms contained in substance *x*. Values for all these parameters for most of the ozone relevant halogen containing gases have been updated recently and the ODP for methyl bromide and many other halogen containing substances have been published (WMO 2002). Using a value of 0.7 years for lifetime of methyl bromide (τ_{total}), and the values listed in WMO (2002) for the other parameters required in equation 2, the ODP is calculated as:

$$ODP(CH_3Br) = 1.12 \cdot 45 \cdot \frac{0.7}{45} \cdot \frac{137.7}{94.4} \cdot \frac{1}{3} = 0.38$$

The ODP of 0.38 listed in the most recent WMO document (WMO 2002) for methyl bromide is significantly lower than previous estimates of 0.65 (Mellouki 1992) and 0.60 (WMO 1994).

The largest source of uncertainty in equation 2 arises from the lifetime of methyl bromide due to uncertainty regarding its potential sources and sinks. The actual amounts of methyl bromide produced and emitted to the environment are highly uncertain as illustrated in table B1 shown in the Appendix B. Uncertainty regarding emissions of methyl bromide from the world's oceans are largest, followed by biomass burning and soil fumigation (Rodriguez and Butler 1996). Oceans may serve as both a source and sink of methyl bromide, depending on the exchange rate of methyl bromide between the water and air. This exchange rate is controlled by both physical properties of the chemical such as its Henry's Law constant, and environmental properties of the ocean and air such as temperature, depth, wind speed, viscosity, and water velocity. Although the air-sea exchange rate of methyl bromide has been studied extensively, any estimate of this rate has an uncertainty on the order of $\pm 50\%$ (Butler and Rodriguez 1996). Uncertainty in the hydroxyl radical concentration (see Section C - Persistence, above) contributes to the uncertainty in the photochemical lifetime of methyl bromide and thus its total lifetime and ODP. Lack of knowledge regarding the role of terrestrial plants as potential sources and sinks also adds to the uncertainty.

(E) GLOBAL WARMING POTENTIAL

The global warming potential (GWP) is the ratio of the warming caused by a substance to the warming caused by a similar mass of carbon dioxide. Mathematically the GWP is given by :

$$GWP(i) = \frac{\int_0^{TH} a_i \cdot [x(t)] dt}{\int_0^{TH} a_r \cdot [r(t)] dt} \quad (3)$$

where TH is the time horizon over which the calculation is based, a_i is the radiative forcing in units of $W/m^2\text{-kg}$ for chemical i , $x(t)$ is the time dependent decay function of chemical i , and the corresponding quantities for the reference gas (usually CO_2) are in the denominator. The radiative efficiencies are related to the amount of infrared (IR) radiation absorbed by the species at 7-14 μm . Since methyl bromide has relatively low absorption intensity in this spectral region its radiative forcing term is small. Furthermore, methyl bromide has a relatively short half-life in comparison to many of the long lived CFCs and the decay function in equation 3 decreases rapidly. This results in a relatively low GWP value and for this reason, methyl bromide is not considered a significant greenhouse gas. The GWP of some common ODP gasses are given in Table 4 (WMO 2002).

Table 3. Direct GWP for some CFCs, HCFCs, and methyl bromide.^a

Chemical	Radiative Efficiency ($W/m^2\text{-ppb}$)	Lifetime (years)	GWP (20 year TH)	GWP (100 year TH)	GWP (500 year TH)
CFC-11	0.25	45	6330	4680	1630
CFC-12	0.32	100	10340	10720	5230
CFC-13	0.25	640	10160	14190	16520
CFC-113	0.30	85	6150	6030	2700
CFC-114	0.31	300	7560	9880	8780
CFC-115	0.18	1700	4990	7250	10040
HCFC-21	0.14	1.7	498	148	46
HCFC-22	0.20	12	4850	1780	552
HCFC-23	0.16	270	9500	12240	10350
HCFC-125	0.23	29	5970	3450	1110
Methyl Bromide	0.01	0.7	16	5	1

^a GWP = global warming potential.

(F) ENVIRONMENTAL LEVELS - MONITORING AND MODELING DATA

Monitoring data for methyl bromide concentrations in soil and air are presented below. Modeling and monitoring data for methyl bromide and bromide in surface and ground water are presented in the Water Resources Assessment (Section 5).

(i) Methyl Bromide Concentrations in Air

Average background concentrations of methyl bromide in air are about 10-26 ppt (40-100 ng/m³) in the Northern hemisphere and about 9-15 ppt (36-60 ng/m³) in the Southern Hemisphere (WHO 1995). Since the widespread use of methyl bromide as a fumigant began, the ambient concentration of atmospheric methyl bromide has increased steadily with an estimated growth rate of about 0.6% annually from 1970 to 1990 (WMO 2002). Urban areas have also had historically high levels of methyl bromide in the atmosphere, primarily due to the use of leaded gasoline. Ethylene dibromide, which is an additive in leaded gasoline, is converted to methyl bromide during the combustion process and released in the exhaust. Tables 4 to 7 summarize the atmospheric levels of methyl bromide monitored at different locations.

Table 4. Ambient air concentrations of methyl bromide.

Concentration (ppt)	Location	Date	Comments	Reference
<5	Pacific Northwest US	1974-1975		Grimsrud and Rasmussen 1975
14.4	Norwegian Arctic	1982-1983		Hov et al. 1984
18,000-55,000	Washington (state)	1976	Auto exhaust using leaded gasoline and no catalytic converter	Harsch and Rasmussen 1977
<10 - 185	Washington (state)	1976	Street with heavy traffic	Harsch and Rasmussen 1977
<10	Washington (state)	1976	Street with light traffic	Harsch and Rasmussen 1977
100	Houston, TX	1980		Singh et al. 1982
81	St. Louis, MO	1980		Singh et al. 1982
124	Denver, CO	1980		Singh et al. 1982
259	Riverside, CA	1980		Singh et al. 1982
84	Staten Island, NY	1981		Singh et al. 1982
41	Pittsburgh, PA	1981		Singh et al. 1982
47	Chicago, IL	1981		Singh et al. 1982

Table 4. Ambient air concentrations of methyl bromide.

Concentration (ppt)	Location	Date	Comments	Reference
20	Minnesota (state)	1990		Pratt et al. 2000
50, 10, 280, 560	Phoenix, Payson, Casa Grande, and Tucson, Arizona; respectively	1994 -1996	Phoenix and Tucson sites represent large metro areas, Payson represents a rural mountain area, and Casa Grande represents a rural/agricultural area	Zielinska et al. 1998

Ambient air levels of methyl bromide are in the ppb range for agricultural communities that employ methyl bromide as a fumigant. Atmospheric concentrations in California communities when fumigation was occurring had peak levels of approximately 2 to 31 ppb (California Department of Pesticide Regulation 2001).

Table 5. Ambient air concentrations near areas of methyl bromide use.

Concentration (ppb)	Location	Date	Distance from application	Reference
1.8 - 30.8	Monterey and Santa Cruz counties, California	2000	Measurements made within areas and periods of most methyl bromide use. Measurements represent 24 hour maximum concentrations.	California Department of Pesticide Regulation 2001.
0.6 - 7.7	Monterey and Santa Cruz counties, California	2000	Average concentration for the study period (Sep 11 - Nov 3)	California Department of Pesticide Regulation 2001
0.3 - 14.2	Kern county, California	2000	Measurements made within areas and periods of most methyl bromide use. Measurements represent 24 hour maximum concentrations.	California Department of Pesticide Regulation 2001.
0.09 - 2.2	Kern county, California	2000	Average concentration for the study period (Sep 11 - Nov 3)	California Department of Pesticide Regulation 2001
0.128 - 1.420	Monterey, CA	1995	Measurements made in an agricultural valley where methyl bromide is frequently used. Measurements represent 24 hour maximum concentrations	Honaganahalli and Seiber 1999

Table 5. Ambient air concentrations near areas of methyl bromide use.

Concentration (ppb)	Location	Date	Distance from application	Reference
1.025	Monterey, CA	1986	Measurements made at 3 sampling sites during a period of peak pesticide usage	Baker et al. 1996
Median = 0.15 95 th ile = 2.50	Oxnard/ Camarillo , California	2001	Measurements made at locations near areas of fumigation during high use period	MRID 45644201
Median = 0.43 95 th ile = 3.80	Santa Maria, California	2001	Measurements made at locations near areas of fumigation during high use period	MRID 45644201

The highest airborne levels of methyl bromide are observed near ground level when agricultural fields, greenhouses or buildings are actively undergoing fumigation. Enclosed fumigations such as the mill and chamber studies had an overall concentration ranged from 27 to 0.012 ppm. Concentrations measured in areas adjacent to or slightly downwind of fumigated field with methyl bromide ranged from 0.001 to 3.35 ppm (Table 6). These studies provide a measure of the potential range of acute exposure concentrations of methyl bromide in air following fumigation. Many environmental factors, including soil properties, temperature gradients, wind direction, and wind velocity can affect volatilization rates and movement of gases in air. Also, fumigation management practices can greatly influence the methyl bromide exposures in the environment. Majewski et al. (1995) conducted two field experiments with fumigant composed of methyl bromide/chloropicrin was injected at a depth of 25-30 cm in liquid form fields located approximately 6 km away from each other. One field was immediately covered with a high barrier plastic tarp while the other field was left uncovered. Both fields were a silty clay loam with similar soil texture, moisture content, and organic matter composition. The peak values are not different from these two methyl bromide application sites (Table 6). However, the volatilization of applied methyl bromide in the tarped field was 4 times lower as compared with the non-tarped field.

Table 6. Air concentrations of methyl bromide from chamber/field fumigations

Concentration (ppm)	Location	Date	Distance from Application	Time of Measurement	Reference
Monitoring data from chamber application					
0.2 - 27.0	ND	ND	Measured 25 m away from mill fumigated with methyl bromide	range of values, 5 - 90 minutes after application	Bond and Dumas 1987

Table 6. Air concentrations of methyl bromide from chamber/field fumigations

Concentration (ppm)	Location	Date	Distance from Application	Time of Measurement	Reference
0.012 - 6.79	No data	1992 - 1993	Measured 2 - 108 meters from stack (aeration method used), 12 - 1262 lbs methyl bromide used in chamber	range of maximum concentrations during 5 - 120 minutes after fumigation	California Department of Pesticide Regulation 2002
0.228	No data	1996	Measured 12 meters from stack (aeration method used), 22 - 32 lbs methyl bromide used in chamber	maximum concentration 12 hours after fumigation	California Department of Pesticide Regulation 2002
Monitoring data from non-tarped field application					
0.001	California	10/92	Measured 40 cm above the field, 392 kg/ha appl rate, non-tarp, injected at 25-30 cm.	peak value measured first day of post-application	Majewski et al., 1995
0.042 - 0.55	California	1992 - 1998	Measured 50 - 300 ft from application, no tarp, shallow injection, 150 - 186 lbs/acre appl rate	range of maximum 24-hour concentrations	California Department of Pesticide Regulation 2002
0.11 - 0.70	California	1993 - 1998	Measured 80 - 600 ft from application, non-tarp, deep injection, 348 - 450 lbs/acre	range of maximum 24-hour concentrations	California Department of Pesticide Regulation 2002
Monitoring data from tarped field application					
0.054 - 0.15	California	1992 - 1998	Measured 25 - 600 ft from application, tarp, shallow injection, 180 - 392 lbs/acre	range of maximum 24-hour concentrations	California Department of Pesticide Regulation 2002
0.092 - 1.7	California	1993 - 1997	Measured 30 - 330 ft from application, tarp, bed application, 160 - 200 lbs/acre	range of maximum 24-hour concentrations	California Department of Pesticide Regulation 2002
<0.022 - 0.634	California	1982	Measured 25 feet downwind from field, no appl rate reported, tarp, injected 8 in below surface	range of hourly averages, 0 - 1 day during/after application	MRID 00159653

Table 6. Air concentrations of methyl bromide from chamber/field fumigations

Concentration (ppm)	Location	Date	Distance from Application	Time of Measurement	Reference
<0.022 - 0.396	California	9/83	Measured 25 - 45 feet downwind from field, no appl rate reported, tarp, injected 8 in below surface	range of hourly averages, 0 - 1 day during/after application	MRID 00159660
0.146 - 0.814	California	8/83	Measured 0 - 1250 feet from starting point of fumigation (all sites on field), no appl rate reported, tarp, injected 8 in below surface	range of hourly averages, 0 - 1 day during/after application	MRID 00159660
0.001	California	10/92	Measured 40 cm above the field, 392 kg/ha appl rate, tarp, injected at 25-30 cm.	peak value measured first day of post-application	Majewski et al., 1995
0.156	California	6/94	Measured 0.5 m above the field, 322 kg/ha appl rate, tarp, injected at 27 inches (68 cm).	peak value measured approximately 1 day post-application	Yates et al. 1997
3.35	California	6/94	Measured 0.5 m above the field, 322 kg/ha appl rate, tarp, injected at 11 inches (28 cm)	peak value measured approximately 1 day post-application	Yates et al. 1997

Differences in concentrations as a function of distance downwind from the site of fumigation are shown in Table 7. In this study, concentrations were measured at different distances from a greenhouse after the soils were fumigated and covered with tarpaulins. Maximum ventilation conditions were created via windows and exhaust systems from the greenhouse. Although, the pattern is decreasing air concentrations as a function of distance from the greenhouse, the maximum concentrations observed occurred at a distance of 10 - 20 meters.

Table 7. Methyl bromide concentrations following fumigation of a greenhouse.^{a, b}

Concentration (ppm)	Measurement Location	Time of Measurement
0.15-4.7	0 - 5 m from greenhouse	Measurements 0 - 24 hours after fumigation
0.20-0.28	5 - 10 m from greenhouse	Measurements 0 - 24 hours after fumigation

Table 7. Methyl bromide concentrations following fumigation of a greenhouse.^{a, b}

Concentration (ppm)	Measurement Location	Time of Measurement
0.12 - 5.7	10 - 20m from greenhouse	Measurements 0 - 24 hours after fumigation
0.05 - 1.4	20 -40 m from greenhouse	Measurements 0 - 24 hours after fumigation
0.025 - 1.5	> 40 m from greenhouse	Measurements 0 - 24 hours after fumigation

^a Application rate of 117 g/m²^b De Vreede et al. 1998

The pattern of air concentrations during and after fumigation over time is an important component of exposure. In the study presented in Table 8, measurements were taken over a 24 hour period during and after fumigation occurred (fumigation time period: 830 - 1700) at an agricultural field at 3 different sites approximately 25 feet from the field. As fumigation activities moved closer to each site, air concentrations peak. The role of wind speed and direction and temperature (e.g., nighttime vs. daytime) may explain the diurnal pattern at different sites. Concentrations are well below 1 ppm throughout the study, but are above the detection limits throughout the 24-hour period of the study. Concentrations remain steady 3 to 4 hours after fumigation ends.

Table 8. Methyl bromide concentrations during and immediately following fumigation at an agricultural field (MRID 00159653).^a

Time	Concentration (ppm)		
	Site 1	Site 2	Site 3
0900 - 0945	0.634	not measured	not measured
1015 - 1100	0.062	not measured	not measured
1115 - 1200	0.437	not measured	not measured
1400 - 1445	not measured	0.257	not measured
1500 - 1545	not measured	0.252	0.122
1600 - 1645	not measured	0.253	0.455
1700 - 1745	not measured	0.284	0.296
1800 - 1845	not measured	0.193	0.317
1900 - 1945	not measured	0.336	0.560
2000 - 2045	not measured	0.455	0.488

Table 8. Methyl bromide concentrations during and immediately following fumigation at an agricultural field (MRID 00159653).^a

Time	Concentration (ppm)		
	Site 1	Site 2	Site 3
2100 - 2145	not measured	0.351	< 0.022

^a Concentrations measured in air at 3 different sites, 25 feet away from field. Fumigation occurred from 0830 to 1700 with one hour break from 1200 to 1300.

(ii) Estimated Methyl Bromide Concentrations in Air

The Industrial Source Complex - Short Term (ISCST) air dispersion model developed by USEPA (USEPA, 1995) was used in estimating atmospheric concentrations of methyl bromide. The ISCST has been used successfully to simulate methyl bromide levels in air following the fumigation of warehouses and agricultural fields located in California (Barry et al. 1997). A large number of air monitoring studies were conducted in California and evaluated for the emission of methyl bromide from treated fields. Based on the air monitoring data of California, CDPR has estimated flux rates under various methyl bromide application methods from fumigated fields.

The modeling approaches used by the Agency were based on 24 hours exposure intervals (i.e., 24 hours time-weighted average of monitored air concentration of methyl bromide). Field sizes includes 1-, 5-, 10-, 20-, and 40 acre squares to represent a cross section of the fields that might be fumigated for agriculture use. ISCST was used in estimating air concentration using field emission ratio (ratio of the flux rate to the application rate), various sized fields, methods of methyl bromide placement, and different meteorological conditions. The basic approaches to estimate air concentrations using ISCST model are outlined in the Health Effects Division's *Draft Standard Operating Procedures (SOPs) for Estimating Bystander Risk from Inhalation Exposure to Soil Fumigant (USEPA, 2003)*. ISCST estimated downwind air concentrations using hourly meteorological conditions that include the wind speed and atmospheric stability.

In this assessment, one set of computations was completed using ISCST model at varying acreage and atmospheric conditions. The lower the wind speed and more stable the atmospheric environment, the higher the air concentrations were observed near the treated areas. The outputs were then scaled to appropriate emission ratios and application rates. Assuming stable weather condition, Figure 2 reflects a wide variety of emission ratios and the concentrations of methyl bromide in air, which also represent differences in such factors as application methods, depth of application, use and type of tarping, field size, and soil characteristics. A maximum concentration of 9.12 ppm (35.58 mg/m³) was estimated using 400 lbs/A application rate, 40 acres field size and 0.80 emission ratio under selected California Department of Pesticide Regulation's (CDPR) methyl bromide application Permit Conditions. Permit conditions and detailed input assumptions and model results were described in the *HED's Draft Chapter on Non-Occupational Risks Associated with Methyl Bromide (USEPA, 2004)*.

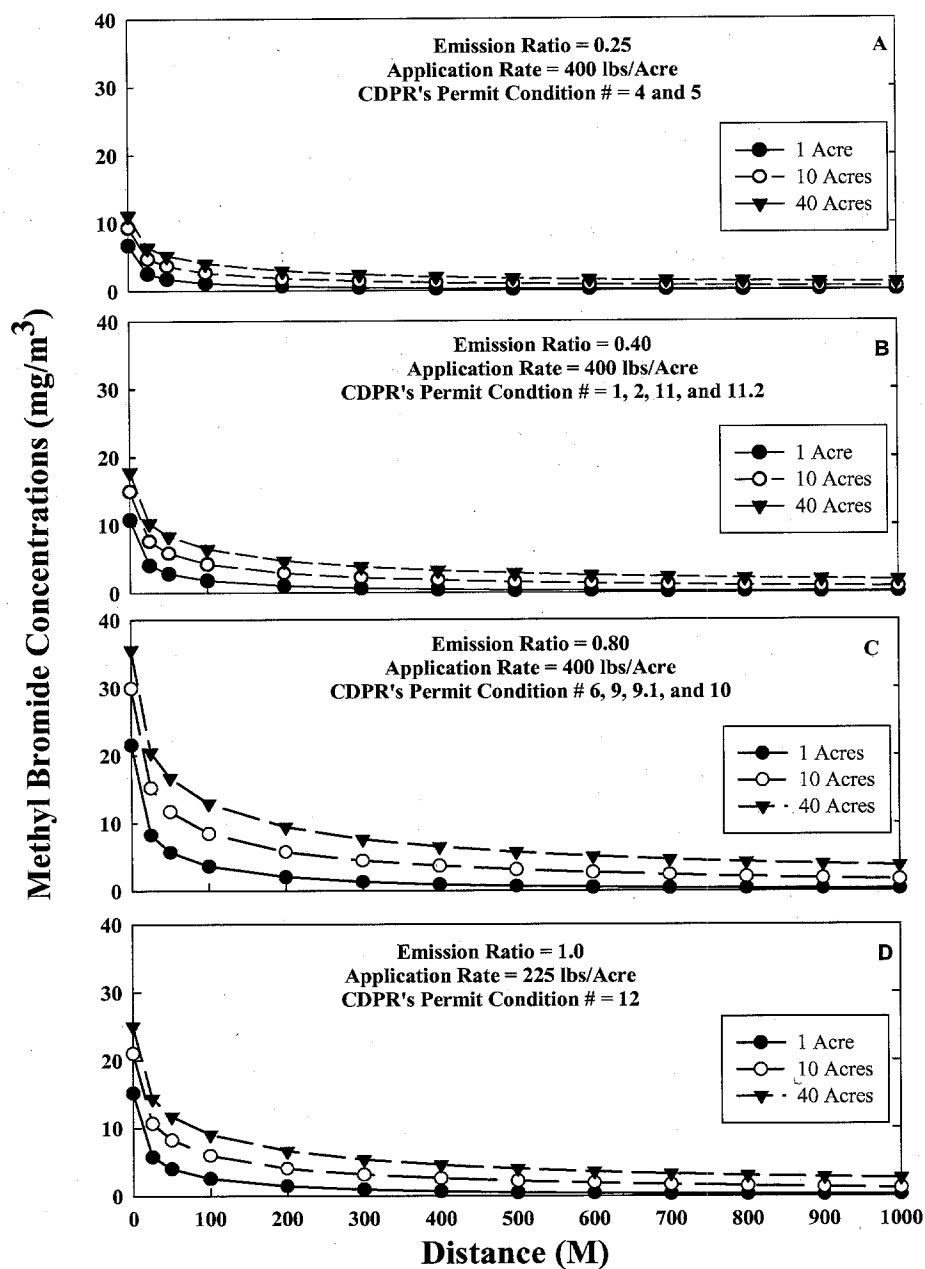


Figure 2. Selected ISCST estimated methyl bromide concentrations under various emission ratios, field sizes, and fumigant application permit conditions for the State of California.

(iii) Bromide Ion Concentrations in Soil and Sediment

Although methyl bromide is widespread throughout the environment, it is rapidly volatilized or degraded in soil, resulting in the release of the bromide ion. The background bromide content of soils normally does not exceed 5 mg/kg bromide ion, although coastal soils may attain levels of 100 mg/kg (WHO 1983). The total bromide ion concentration in 2 soils containing 2.81% and 0.93% organic carbon was 9 and 5 mg/kg, respectively, before application of methyl bromide (IARC 1986). Following the application of methyl bromide at a rate of 500 mg/kg to both soils, the bromide ion concentration increased to 63 mg/kg for the soil containing 2.81% organic carbon and 25 mg/kg for the soil containing 0.93% organic carbon after 24 hours (IARC 1986). The World Health Organization summarized experiments in which the bromide ion concentrations were measured in greenhouse soil before and after the application of methyl bromide (80 g/m²). Before fumigation, bromide levels were about 5 mg/kg. Two months after treatment, bromide levels of over 30 mg/kg were measured. After a further 3 months, levels had decreased to less than 10 mg/kg.

Evidence of uptake of bromide ion by plants and vegetables is available. In order to assess the uptake of bromide ion by crops, a level open air plot (clay-loam, 12 percent organic matter) was fumigated with methyl bromide at 100 g/m² and left covered for five days (WHO 1983). Three days after the end of fumigation the fumigated plot and an adjacent untreated plot were marked off into micro-plots 1.25 m × 1.25 m. The plots were then planted with crops, at commercial densities, for the next 18 months. Lettuce harvested approximately 12 weeks after fumigation contained between 146 and 458 mg/kg bromide ion/lettuce (fresh weight) with a mean value of 305 mg/kg; controls ranged from 3 to 7 with a mean value of 4. Lettuce planted one year after fumigation contained approximately seven times the background level. Spring cabbage harvested 10 months after fumigation contained 93 to 182 (mean value 127) mg/kg bromide ion/cabbage (fresh weight); for 'January King' cabbage harvested 18 months after fumigation, the range was 73 to 139 (mean value 106). The cabbage controls ranged from 3 to 9 mg/kg bromide ion (WHO 1983).

Bromide has been found in lake and river sediments heavily affected by human activities including agricultural and industrial uses. Sediment concentrations of bromide ion ranged between 5 - 25 ppm in Lake Nahuel Huapi, Argentina (Guevara et al. 2002) and 5.4 - 16.9 ppm in Zarka River, Jordan (Al-Jundi 2000). Concentrations of bromide ion ranged between 9 - 18 ppm over the years 1920 to 2000 in several lakes in the Danube Delta of Europe (Dinescu and Duliu 2001). The peak concentrations of 16 - 18 ppm occurred around 1965 and end of 1980's. These higher concentrations were correlated with industrial activities that were particularly intense in Central and Eastern Europe before 1990. The sediment concentrations reported in these studies did not identify specific sources so it is not clear if they represent degradation from methyl bromide fumigation or from automobile exhaust gases, another potential source of bromide ions.

V. WATER RESOURCE ASSESSMENT

Henry's Law constant ($744 \text{ Pa}\cdot\text{m}^3/\text{mol}$) of methyl bromide suggest that rapid volatilization of methyl bromide from water and soil surfaces is expected to be an important process. Monitoring data confirming the presence of methyl bromide in air, soil, and sediment are presented above. In this section, estimated concentrations in water are presented. Since Tier I models FIRST and GENEEC are not appropriate in estimating concentrations of the vapor phase of methyl bromide, Tier II PRZM/EXAMS was used in estimating methyl bromide concentrations in surface water. Additional chemical specific physical parameters DAIR (vapor phase diffusion coefficient) and ENPY (enthalpy of vaporization) were activated during the PRZM-EXAMS simulation. Chemical Application Method (CAM) of 4 was used in simulating subsurface application of methyl bromide assuming its uniform distribution within 25 cm. Four field scenarios - California tomatoes, California grapes, Florida strawberries, and North Carolina tobacco were used in estimating EDWCs and EECs. FIRST and GENEEC were used in estimating bromide ion (a major degradate of methyl bromide) concentrations in surface water. Tier I SCIGROW is not an appropriate model to estimate the concentrations of a vapor phase of methyl bromide and its inorganic degradate bromide ion in groundwater.

(A) Tier II PRZM/EXAMS Modeling (Surface Water)

Estimated environmental concentrations (EEC) of methyl bromide in surface waters were calculated using PRZM v.3.12 (Pesticide Root Zone Model), which simulates runoff and erosion from the agricultural field, and EXAMS v.2.98 (Exposure Analysis Modeling System), which simulates environmental fate and transport in surface water. A graphical user interface developed by EPA (<http://www.epa.gov/oppefed1/models/water/>) was employed to enter the input values for each model run. Four PRZM field scenarios were used in the modeling exercise: California tomatoes, California grapes, Florida strawberries, and North Carolina tobacco. An index reservoir from Illinois was used to determine estimated drinking water concentrations (EDWCs) while a Mississippi pond scenario was used to determine estimated environmental concentrations (EEC) for ecological risk assessment. Each described a generic scenario for the EXAMS portion of the modeling exercise. Important input parameters used for the PRZM/EXAMS modeling are shown in Table 9.

There is an uncertainty in estimating methyl bromide exposure in water bodies due to post-application tarping of the treated area. If tarping is used to minimize the volatilization of methyl bromide, the loading of the chemical through runoff will be limited until the tarp is sliced or removed from the field. The present version of PRZM model has limited capabilities in capturing the load of applied chemical under a post-application tarp scenario. Therefore, the estimated concentrations of methyl bromide in water bodies may be upper bound since the load of methyl bromide from runoff is considered in the PRZM/EXAMS simulation.

PRZM/EXAMS simulates 30 years of weather at each application site in order to estimate the impact of variable weather on pesticide runoff from a treated field to an adjacent water body. To

provide a conservative assessment that is consistent from crop to crop and from chemical to chemical, the maximum one-in-ten-year return period concentration value is chosen to represent the duration of concentration which corresponds to each relevant toxicity endpoint. EFED recognizes that methyl bromide is applied once in every 22 years to vineyards. However, the simulated EDWCs and EECs values estimated in this assessment for different scenarios correspond to the methyl bromide concentrations that are expected to be equaled or exceeded only one out of every ten applications. The surface water concentrations at these sites have a one-in-ten chance to be greater than estimated values and a nine-in-ten chance of being less than the estimated values due to the variability of the weather.

Table 9. PRZM/EXAMS Input Parameters for Methyl Bromide

Parameters	Values & Units	Sources
Molecular Weight	94.94 g Mole ⁻¹	Tomlin, 1994
Vapor Pressure 25°C	1620 mm Hg @ 25°C	Dauber and Danner 1989
Water Solubility @ pH 7.0 and 25°C	15200 mg/L @ 25°C	Tomlin, 1994
Henry's law constant	0.007 atm-m ³ /mol	Yates and Gan 1998
DAIR	6944 cm ² /day [†]	Fuller et al., 1966
ENPY	5.49 kcal/mole (22.81 kJ/mol)	Chickos and Acree, 2003
Hydrolysis Half-Life (pH 7)	11 days	MRID 42720201
Aerobic Soil Metabolism t _{1/2}	22 days (90% upper conf. bound on 6 values).	Papiernik et al., 2000 Gan and Yates, 1996
Aerobic aquatic metabolism [‡]	15 day	Goodwin et al 1988
Direct Aqueous Photolysis	9.0 days	MRID 42720301
Soil Water Partition Coefficient (K _{oc})	18.0 L Kg ⁻¹ (mean of 4 values)	Daelemans and Siebering (1977)

CROP MANAGEMENT

Crops and application Rates	Application Date*	Sources
Florida Strawberry @ 448 kg/ha	August 15	Application rates are obtained from current labels of methyl bromide.
California Tomato @ 448 kg/ha	January 15	
California Grapes @ 448 kg/ha	January 15	
North Carolina Tobacco @ 959 kg/ha	February 15	

Table 9. PRZM/EXAMS Input Parameters for Methyl Bromide

Parameters	Values & Units	Sources
Application Method	Ground Injection CAM = 4 Depth of Incorp = 25cm	Standard assumptions according to the Guidance for selecting input parameters in modeling for environmental fate and transport of pesticides. Version II. December 4, 2001.
Spray Efficiency	100%	
Spray Drift	None	

† = Calculated using $1.55/\text{molecular mass of methyl bromide}^{0.65}$ (cm^2/s)

‡ = Selected input parameters were multiplied by 3 according to Guidance for selecting input parameters in modeling for environmental fate and transport of pesticides. Version II. February 28, 2002.

* = Application dates are obtained from OPP's Biological & Economic Analysis Division

(i) Estimated Drinking Water Concentration (EDWC) of Methyl Bromide

The estimated drinking water concentrations (EDWCs) in surface waters derived from Tier II PRZM/EXAMS simulation employing the index reservoir scenario are summarized in Table 10 for Florida Strawberry, which yielded the highest values of all the scenarios. Estimated drinking water concentrations for California tomatoes, California grapes, and North Carolina Tobacco were also investigated but gave consistently lower EDWCs as compared to Florida Strawberry (results were not included). The assessments were based on maximum application rates for methyl bromide. A complete summary of the model input and output is presented in Appendix C, along with a discussion of the methodology used to calculate the concentration associated with the 1-in-10 year probability of exceedance equal to 10 percent. These values generally represent upper-bound estimates of the concentrations that might be found in surface water due to the use of methyl bromide.

EFED could not estimate the groundwater concentration of methyl bromide because EFED does not currently perform vapor phase transport of fumigants to groundwater. Based on the data base of pesticides in groundwater (U.S. EPA, 1992), 2 wells in California (out of 20,429 wells monitored in Florida, California, and Hawaii) had methyl bromide levels from 2.5 - 6.4 $\mu\text{g/L}$.

(ii) Estimated Drinking Water Concentration (EDWC) of Bromide ion

Bromide ion, a major degradate of methyl bromide can contribute surface water contamination through runoff and erosion from the methyl bromide application sites to nearby surface water bodies. The potential for bromide ion residues to contaminate surface water sources of drinking

water assessed with the Tier I FIRST (FQPA Index Reservoir Screening Tool) model. The modeled drinking water source is the Shipman city reservoir in Illinois. The single application rate of bromide ion was adjusted from the proposed highest rate of methyl bromide for tobacco proportionally to the minimal volatilization relative to the total amount applied methyl bromide and to their molecular weight. It was also assumed that it has the same solubility like parent methyl bromide, and no adsorption to soils as well as stable in the environment. Input parameters used in the FIRST model are listed in Table 10. The FIRST generated EECs of bromide ion are considered to be upper-bound concentrations may occur in the surface water bodies near methyl bromide application sites.

Table 10. FIRST Input Parameters for Bromide ion

Parameters	Values & Units	Sources
Water Solubility @ pH 7.0 and 25°C	15200 mg/L @ 25°C	Tomlin, 1994
Hydrolysis Half-Life (pH 7)	Stable	Standard assumptions
Aerobic Soil Metabolism $t_{1/2}$	Stable	
Aerobic aquatic metabolism	Stable	
Direct Aqueous Photolysis	Stable	
Soil Water Partition Coefficient (Koc)	None	

CROP MANAGEMENT

Crops and application Rates[‡]

North Carolina Tobacco @ 575 lb/A	1 application
Application Method	Ground Injection (CAM = 4) Depth of Incorp = 6 inches
Spray Efficiency	100%
Spray Drift	None
PCA (For FIRST model only)	0.87

[‡] = Highest methyl bromide application rate x [(0.80, the maximum potential conversion rate of degradation of methyl bromide to bromide ion, assuming minimal 0.20 volatilize) x (0.84, the molecular weight ratio of bromide ions to methyl bromide)]

(iii) Groundwater Monitoring For Drinking Water Assessments

The EDWCs of methyl bromide and bromide ion were not estimated using Tier I SCIGROW model. SCIGROW is not an appropriate model to estimate the concentrations of a vapor phase and inorganic ions transport to groundwater. Based on the data base of pesticides in groundwater (U.S. EPA, 1992), 2 wells in California (out of 20,429 wells

monitored in Florida, California, and Hawaii) had methyl bromide levels from 2.5 - 6.4 µg/L. The primary degradation products of methyl bromide are methanol and bromide ion. Bromide ion may persist longer in water than methyl bromide and potentially accumulate in water bodies. Bromide ion was detected in surface water samples monitored by the USGS (USGS NAWQA). Surface water concentrations ranged from 0.061 to 15.59 mg/L and were detected in two sampling sites only, Riverside and San Bernardino counties, California. Samples were collected intensively over a 2 day period in May 2001 and 2002. The bromide ion was also detected in groundwater samples monitored by the USGS (USGS NAWQA). Groundwater concentrations ranged from 0.015 to 0.766 mg/L. The EDWCs to be used for human health risk assessments are presented in Table 11, but a more complete presentation of the results of PRZM/EXAMS and FIRST models data and as well as monitoring are given in Appendix C and Appendix D respectively.

Table 11. Methyl bromide and bromide ion in surface water and groundwater

Chemical	Surface Water (µg/L)		Groundwater (µg/L)
	Acute	cancer chronic	
Methyl	357 ^a	1.0 ^a	6.4 ^b
Bromide ion	8,748 ^c	6,273 ^c	766 ^d

^a Based on 1-in-10 year exceedance probability (0.10). Values reflect output from PRZM/EXAMS multiplied by the percent crop area applied (0.87) for Florida Strawberry scenario.

^b Recommended EDWCs values for acute and chronic for groundwater (monitoring data)

^c Recommended EDWCs values for acute and chronic for surface water. Values Reflect output from FIRST multiplied by the percent crop area applied (0.87) for North Carolina Tobacco scenario.

^d Recommended EDWCs values for acute and chronic for groundwater.(monitoring data)

(iv) Estimated Environmental Concentration (EEC) of methyl bromide for Ecological Risk Assessment

Estimated Environmental Concentrations (EECs) used to determine acute and chronic risks to aquatic organisms were estimated using four crop scenarios (California tomato, Florida strawberry, California grape, and North Carolina tobacco) and the standard Mississippi Pond scenario.

Table 12. Surface water EECs µg/L) for ecological risk assessment based on methyl bromide use on various crops.^a

Crop	Application Rate kg/ha	Number of Applications	Peak (24 Hour)	96 Hour	21 Day	60 Day	90 Day	Annual
California, Tomato	448 kg/ha	1	161.38	107.72	35.20	13.74	9.16	2.25

Table 12. Surface water EECs $\mu\text{g/L}$ for ecological risk assessment based on methyl bromide use on various crops.^a

Crop	Application Rate kg/ha	Number of Applications	Peak (24 Hour)	96 Hour	21 Day	60 Day	90 Day	Annual
Florida, Strawberry	448 kg/ha	1	171.3	93.54	28.98	10.23	6.84	1.69
California, Grape	448 kg/ha	1	51.70	34.42	11.03	3.90	2.60	0.64
North Carolina, Tobacco	959 kg/ha	1	45.29	31.38	15.09	5.44	3.63	0.89

^a Based on 1-in-10 year exceedance probability (0.10).

Results of the 1-in-10 year probabilities are summarized in Table 12 and the full set of EECs are given in Appendix C. In addition, the method for calculating a 1-in-10 year EEC is described in Appendix C. The EECs presented in Table 12 were used in this ecological risk assessment.

The important output parameters for the modeling exercises are the peak, 96 hour, 21 day, 60 day, 90 day and yearly methyl bromide levels estimated in the model reservoir and pond. These data are shown in the accompanying EXCEL spreadsheets as well as Appendix C. The highest EECs were observed for the California tomatoes and Florida strawberries scenarios. The large variation of methyl bromide levels estimated in surface waters can be traced to chemical loadings into either the environmental pond or index reservoir from the PRZM output. Since the chemical input parameters are identical in each PRZM run, the different outputs are entirely dependent upon the different soil parameters used in the corresponding crop scenarios during the PRZM portion of the modeling exercise, as well as the scenario-specific meteorological data. A much higher percentage of pesticide was leached below the root zone level for the North Carolina tobacco and California grapes scenarios as compared to the California tomatoes and Florida strawberries scenarios due to a number of factors such as slope, soil type, moisture content, and the runoff curve numbers used for the different fields. This resulted in runoff and erosion flux vectors for the North Carolina tobacco and California grapes that were considerably lower than those estimated from the California tomatoes and Florida strawberries scenarios. As a consequence, the methyl bromide loadings into the EXAMS model environment were much lower, resulting in the smaller EECs.

(v) Estimated Environmental Concentration (EEC) of bromide ion for Ecological Risk Assessment

Estimated Environmental Concentrations (EECs) for bromide ion in the standard pond were generated with the Tier I GENEEC 2.0 model. The model inputs were the same as the FIRST model described in the Table 10 for drinking water assessment. The GENEEC generated EECs

of bromide ion are considered to be upper-bound concentrations may occur in the surface water bodies near methyl bromide application sites. The EECs presented in Table 13 were used in this ecological risk assessment. GENEEC output is presented in Appendix C.

Table 13. Surface water EECs (mg/L) of bromide ion for ecological risk assessment of based on methyl bromide use on North Carolina Tobacco.

Crop	Application Rate	Number of Applications	Peak (24 Hour)	96 Hour	21 Day	60 Day	90 Day	Annual
North Carolina, Tobacco	575 lb/A	1	5.38	5.38	5.38	5.38	5.38	5.38

(B) Monitoring Data - Methyl Bromide and Bromide Ion Concentrations in Water

(i) Surface Water

The natural background concentration of methyl bromide in the oceans is in the ppb range. Monitoring data from 30 different global latitudes resulted in an average methyl bromide concentration of 1.2 ppb (U.S. EPA 1986). Slightly higher levels were detected off the coast of England (2.5-6.5 ppb), while lower levels (0.14 ppb) were observed off the coast of California (U.S. EPA 1986).

Methyl bromide levels are expected to be highest in streams or ponds that receive runoff from agricultural fields that have recently been fumigated with methyl bromide. Surface water in a greenhouse crop growing region of Malines-Antwerp, Belgium was sampled for the presence of bromide ion before, during, and after fumigation with methyl bromide. The maximum concentration of bromide ion in a brook downstream was reported as 9.6 ppm (IARC 1986). In nearby rivers, only a slight increase in the level of bromide ion was observed suggesting that the amount of methyl bromide contained in runoff leading to these waterways was small. The concentrations of methyl bromide and bromide ion were measured in irrigation water, drainage water, and surface water during the leaching periods in two Netherlands glasshouse soils after fumigation with methyl bromide (WHO 1995). Maximum concentrations in drainage water, determined within 24 hours of the start of leaching, were 9.3 ppm (methyl bromide) and 72 ppm (Br) (WHO 1995). Studies of the bromide ion concentrations in precipitation, surface water, and ground water in a horticultural district in the Netherlands in 1979-80 gave maximum values of 0.98, 41, and 17 ppm respectively, the highest concentrations being found during the main fumigation/leaching time in September-October 1979 (WHO 1995). The bromide ion was detected in surface water samples monitored by the USGS (USGS NAWQA). Surface water concentrations ranged from 0.061 to 15.59 mg/L and were detected in two sampling sites only, Riverside and San Bernardino counties, California. Samples were collected intensively over a 2

day period in May 2001 and 2002. Methyl bromide and bromide ion concentrations in surface waters are summarized in Table 14.

Table 14. Concentrations of methyl bromide or bromide ion in surface waters.

Chemical	Concentration	Location	Source
Methyl bromide	9.3 ppm	Drainage water near a fumigated greenhouse in Netherlands	WHO 1995
	1.2 ppb	Average background level in oceans	U.S. EPA 1986
Bromide ion	72 ppm	Drainage water near a fumigated greenhouse in Netherlands	WHO 1995
	41 ppm	Surface water in a horticultural area	WHO 1995
	9.6 ppm	Maximum concentration in brook downstream of fumigated greenhouse in Belgium	IARC 1986
	0.98 ppm	Rainfall in a horticultural area	WHO 1995
	0.061 - 15.59 ppm	Surface water from monitoring sites; agricultural, urban, and mixed land uses	USGS NAWQA 2004

(ii) Ground Water

An analysis of the EPA STORET (Storage and Retrieval) database indicated that methyl bromide was infrequently detected in ambient water samples (1.4% of 941 samples) (Staples et al. 1985).

Methyl bromide is monitored in groundwater and surface water as part of the United States Geological Survey National Water Quality Assessment Program (NAWQA). A study summarizing NAWQA data from 1985 - 1995 found methyl bromide in 0.1% of the 2,948 groundwater sites sampled. Sites were selected to represent ambient water quality conditions. The maximum groundwater concentration was 0.5 ppb sampled in a rural watershed. The study did not state which watershed this was or whether it was impacted by agricultural activity.

Another study summarizing NAWQA data from 1992 to 1996 (Kolpin et al. 2000) reported detectable concentrations of methyl bromide in groundwater at a handful (i.e., 0.06%) of the 1,831 sampling sites. These sampling sites included domestic and public supply wells as well as springs and tile drains. The maximum concentration was 0.5 ppb.

USGS (<http://water.usgs.gov/nawqa/>) provides monitoring data on methyl bromide concentrations in water. No detectable concentrations were found in surface water (250 sites monitored), however, methyl bromide was detected in groundwater in 3 different watersheds. The complete data set is presented in Appendix D. Concentrations ranged from 0.10 - 0.50 ppb in urban and mixed-land use watersheds in Benton, Idaho, Richland, South Carolina, and Jefferson, Georgia, respectively. Detection frequencies for methyl bromide in wells at active and

abandoned hazardous waste sites were reported for different EPA regions of the United States (Plumb 1992). In EPA Region 3 (Pennsylvania, West Virginia, Maryland, District of Columbia, and Delaware), methyl bromide was detected in 3.2% of the wells, while in EPA Region 9 (California, Nevada, Utah, Hawaii, Guam, Samoa, Northern Mariana Islands, and Trust Territories) it was detected in 0.8% of the wells. The bromide ion was detected in groundwater samples monitored by the USGS (USGS NAWQA). Groundwater concentrations ranged from 0.015 to 0.766 mg/L. In a comprehensive study of groundwater throughout the United States, EPA reported that methyl bromide was detected in only 2 out of 20,429 groundwater wells sampled from 1971-1991 (EPA 1992). Methyl bromide was not detected in any groundwater samples adjacent to fields that had been fumigated with this compound in 12 California wells (MRID 00152338) and 19 groundwater wells located in Florida (MRID 00152337). A table of all detected concentrations of bromide and methyl bromide in surface and groundwater is included in Appendix D of this report.

VI. ECOLOGICAL HAZARD DATA

(A) Summary

The ecotoxicity database on terrestrial and aquatic organisms for methyl bromide and the bromide ion was reviewed, including both MRID submissions and studies from the open literature. Based on review of the literature, information is available to quantitatively assess the risk of methyl bromide exposure in mammals, birds, fish, aquatic invertebrates and algae. Since methyl bromide is highly volatile and is a gas at room temperature and standard pressure, inhalation of vapor following soil fumigation is the major exposure pathway for non-target mammals and birds. Exposure may also occur through ingestion of contaminated water, although this is considered a minor exposure pathway. Toxicity endpoints that will be used to characterize risk quantitatively are summarized in Table 15. Although the efficacy of methyl bromide in the control of target microorganisms and terrestrial invertebrates has been extensively studied, the available data on non-target terrestrial invertebrates, microorganisms and plants are qualitative in nature and do not provide sufficient data to allow for the quantitative assessment of risk. There is no information available on the effects of methyl bromide in rooted aquatic plants.

In water, the bromide ion is one of the primary degradation products of methyl bromide. As an element, the bromide ion may persist longer in water than methyl bromide, possibly resulting in the accumulation of the bromide ion in water. Comparison of toxicity values for methyl bromide and the bromide ion (Table 16) obtained in the same species for the same exposure periods show that the bromide ion is far less toxic than methyl bromide, by factors ranging from approximately 1,390 to 34,000. Although the relative potency of the bromide ion is extremely low compared to methyl bromide, the risk of exposure of aquatic species to the bromide ion will also be considered. Toxicity endpoints for bromide ion in aquatic species are summarized in Table 17.

Table 15. Summary of toxicity values for methyl bromide.

Exposure Scenario	Species	Exposure Duration	Toxicity Reference Value	Reference
Mammals				
Acute oral ^a	rat	Single oral dose in corn oil by gavage	LD ₅₀ = 86 mg/kg body wt (females) (moderately toxic)	MRID 43510301
Chronic oral ^b	rat	Diet	NOAEL = 2.2 mg/kg/day (decreased body weight, weight gain and food consumption)	MRID 44462501 Guideline/ acceptable
Acute inhalation ^c	rat	4-hours	LC ₅₀ = 780 ppm (equivalent to 3.03 mg/L)	Kato et al. 1986
Chronic inhalation ^d	dog	5- to 7- weeks	LOAEL = 5.3 ppm (1.43 mg/kg/day) NOAEL < 5.3 ppm (lowest dose tested)	MRID 43386802 acceptable/ non-guideline
Birds				
Acute oral	bobwhite quail	Single oral dose by gavage in peanut oil	LD ₅₀ = 73 mg/kg body wt (moderately toxic)	MRID 43085901 Core Study ^h
Chronic oral, Acute and Chronic inhalation	—	No data		—
Fish				
Acute ^e	rainbow trout	96-hours, static conditions	LC ₅₀ = 3.9 ppm (moderately toxic)	MRID 43066701 Supplemental Study ^h
Chronic	guppy	1-month	NOAEC = 0.1 ppm (general signs of toxicity)	Webster and Vos 1994
Aquatic Invertebrates				
Acute ^f	<i>Daphnia magna</i>	48-hours, static conditions	LC ₅₀ = 2.6 ppm (moderately toxic)	MRID 42932901 Core Study ^h
Chronic	—	No data		—
Algae				
Acute ^g	<i>Scenedesmus quadricauda</i>	24-hours	LC ₅₀ = 2.2 ppm	Canton et al. 1980

Table 15. Summary of toxicity values for methyl bromide.

Exposure Scenario	Species	Exposure Duration	Toxicity Reference Value	Reference
<p>^a The RfD for acute exposure is based on an inhalation teratology study in rabbits (MRID 41590401), using a NOAEL of 40 ppm (14 mg/kg/day) for signs of maternal neurotoxicity (EPA 2003). No treatment-related mortalities occurred in this study. Use of LD₅₀ values, rather than NOAELs, to assess risk of acute exposure in terrestrial animals is in accordance with guidance in the EFED Training Manual (EFED 2001).</p> <p>^b The NOAEL of 2.2 mg/kg/day was used to establish the chronic RfD (EPA 2003).</p> <p>^c In the HED HIARC report (EPA 2003), the LOAEL of 5.3 ppm obtained in the 5- to 7-week exposure study in dogs (MRID 43386802) was used to assess the risk of acute inhalation exposure. Use of LD₅₀ values, rather than NOAELs, to assess risk of acute exposure in terrestrial animals is in accordance with guidance in the EFED Training Manual (EFED 2001).</p> <p>^d In the HED HIARC report (EPA 2003), the LOAEL of 5.3 ppm obtained in the 5- to 7-week exposure study in dogs (MRID 43386802) was used to assess the risk of chronic inhalation exposure.</p> <p>^e A slightly lower 96-hour LC₅₀ value of 0.7 ppm was obtained from a study in medaka (Canton et al. 1980). However, this study appears to be an internal report that was not published in the peer-reviewed literature. Thus, the data from rainbow trout (MRID 43066701, a Supplemental Study) will be used to assess acute risk in fish.</p> <p>^f A slightly lower 48-hour LC₅₀ value of 2.2 ppm was obtained from a study in daphnia (Canton et al. 1980). However, this study appears to be an internal report that was not published in the peer-reviewed literature. Thus, the data from MRID 43066701 (a Core Study) will be used to assess acute risk in aquatic invertebrates.</p> <p>^g Data on the toxic effects of methyl bromide to algae are only available from a single study (Canton et al. 1980), which appears to be an internal report and not published in the peer-reviewed literature.</p> <p>^h Core = satisfies guidelines; supplemental = study is scientifically sound, but does not satisfy guidelines.</p>				

Table 16. Comparison of toxicity values for methyl bromide and bromide ion in aquatic species.

Species	Exposure	Toxicity Reference Value (TRV) (mg/L)			Relative Potency ^a
		Methyl Bromide	Bromide Ion ^e	Endpoint	
guppy	acute	0.8 ^b	16,000	96-hour LC ₅₀	20,000
	chronic	0.1 ^c	2,500	1-month NOAEC	25,000
medaka	acute	0.7 ^b	24,000	96-hour LC ₅₀	34,286
	chronic	0.56 ^c	780	1-month NOAEC	1,393
daphnia	acute	2.6 ^d	11,000	48-hour LC ₅₀	4,230
	chronic	no data	7.8	23-day NOAEC (impairment of reproduction)	—
green algae (<i>Scenedesmus quadricauda</i>)	NA	3.2 ^b	7,800	48-hour LC ₅₀	2,438

^a Ratio of bromide ion TRV divided by methyl bromide TRV.
^b Canton et al. (1980).
^c Webster and Vos (1994).
^d MRID 42932901.
^e Canton et al. (1983).
 NA = not applicable.

Table 17. Summary of toxicity values for bromide ion.^a

Exposure Scenario	Species	Toxicity Reference Value	
		Value (mg Br ⁻ /L)	Endpoint
Fish			
Acute exposure	guppy	16,000	96-hour LC ₅₀
Chronic exposure	guppy	7.8	124-day NOAEC (reproductive effects)
Aquatic Invertebrates			
Acute exposure	<i>Daphnia magna</i>	11,000	48-hour LC ₅₀
Chronic exposure	<i>Daphnia magna</i>	7.8	23-day NOAEC (impairment of reproduction)
Algae			
Acute exposure	<i>Scenedesmus quadricauda</i>	10,000	96-hour LC ₅₀
^a Source: Canton et al. (1983).			

(B) Effects in Target Organisms

The use of methyl bromide as a soil and space fumigant in the control of fungi and other soil pathogenic microorganisms, nematodes, weeds, and rodents has been extensively studied. Study details are provided in Appendix A4. Results show that methyl bromide has a broad spectrum of activity in controlling crop and stored commodities pests and that the response of target organisms is highly dependent upon experimental and environmental conditions.

Methyl bromide is used to control a large variety of terrestrial invertebrate species, including nematodes, beetles, termites, weevils, moths and mites. Nearly all of the available information on the effects of methyl bromide in terrestrial invertebrates was obtained from greenhouse and field studies in target organisms. Based on the results these studies, the susceptibility of terrestrial invertebrates to methyl bromide appears to be highly variable, even for different strains of the same species (Bell 1988). Given the large number of variations in experimental protocols and the uncontrolled nature of field studies, it is difficult to compare study results or draw firm conclusions regarding species sensitivities among target organisms. However, in general, susceptibility to methyl bromide appears to increase with increasing temperature (Abdalla and Lear 1975, Bell 1988) and to depend upon the growth stage of the organism, with eggs generally more tolerant than larval, pupal or adult stages (Adu and Muthi 1985, Dentener et al. 1998, El-

Buzz et al. 1974, Hole 1981, Macdonald and Mitchell 1996, Mostafa and Kamel 1972, Zettler et al. 2002).

Results of greenhouse and field studies show that methyl bromide is highly effective in controlling many pathogenic fungal species (MRID 00010245, MRID 00013029, MRID 00013030, MRID 00013161, MRID 00013163, MRID 00013174, Bourbos and Skoudridakis 1991, Enebak et al. 1988, 1990, Filip and Roth 1977, Hartill and Campbell 1973, Le Roux 1998, Thomason 1959, Vanachter 1974, Weihing et al. 1971, Wells and Payne 1975, Weststeijn 1973, Winstead and Garriss 1960). Under most experimental conditions using recommended application rates, eradication of the target fungal species was complete or nearly complete. Recovery of fungal populations was variable and dependent upon experimental and environmental conditions. Fungal populations remained substantially decreased for up to nine months after a single application of methyl bromide (Enebak et al. 1988, 1990); however more rapid re-colonization has also been reported (Bourbos and Skoudridakis 1991). In addition to fungi, methyl bromide is also effective in controlling mold and pathogenic bacteria and viruses (MRID 00013030, Ito et al. 1972, Richardson and Monro 1965, Strider 1975). Although results of these efficacy studies show variability among species regarding sensitivity to methyl bromide, given the variation in study protocols and experimental conditions, it is difficult to compare study results.

Compared to the large number of efficacy studies on target terrestrial invertebrates and soil microorganisms, much less information is available on the effectiveness of methyl bromide in the control of weeds. As summarized in Appendix A4, when applied at recommended rates, methyl bromide is effective in controlling a variety of weeds without producing damage to non-target crops. As discussed in Section 6(D)(i) and summarized in Appendix A3, the response of non-target plants is highly variable and depends upon experimental conditions; thus, it is likely that response of target plants to methyl bromide also exhibits variability.

(C) Toxicity to Terrestrial Animals

(i) Mammals, Acute and Subacute

The toxicity of methyl bromide to mammalian species has been extensively studied in laboratory mammals; recently, these studies were reviewed by the Health Effects Division (HED) Hazard Identification Assessment Review Committee (HIARC) (U.S. EPA 2003, Appendix F). The acute and chronic toxicity of methyl bromide in laboratory mammals has been well characterized and RfDs have been determined for both acute and chronic dietary exposure. The acute dietary RfD for the general population is based on the NOAEL of 90 mg/kg/day for decreased activity; data were obtained from an acute inhalation study in rats (MRID 42793601). The acute dietary RfD for females is based on an NOAEL of 14 mg/kg/day for maternal toxicity and fetal malformations in rabbits following gestational inhalation exposure (MRID 41580401). However, LD₅₀ values were not obtained in these studies, as no treatment-related mortalities occurred in either study. Thus, for this risk assessment, the risk of acute oral exposure will be

assessed using the LD₅₀ value of 86 mg/kg obtained from a single dose gavage study in female rats (MRID 43510301). Details of this study are provided in Appendix A1.

Details of inhalation studies in laboratory mammals are provided in Appendix A1. Acute inhalation exposure of rats to methyl bromide concentrations up to 350 ppm for 6 hours did not result in any treatment related mortalities (MRID 42793601); thus, an LC₅₀ value could not be determined from this study. Therefore, the open literature (Kato et al, 1986) LC₅₀ value of 780 ppm (3.03 mg/L), reported in the HED HIARC report will be used to assess the risk of acute inhalation exposure of mammals. For the risk of chronic inhalation exposure, the LOAEL of 5.3 ppm (equivalent to 1.43 mg/kg/day) obtained from a 7-week inhalation study in dogs (MRID 43386802) will be used.

(ii) Birds, Acute and Subacute

Very little information is available regarding the effects of methyl bromide exposure to avian species. The results of a single study of acute exposure via gavage yield an LD₅₀ value in bobwhite of 73 mg a.i./kg, with an NOAEC for mortality of 31.3 mg a.i./kg; study details are provided in Appendix A1 (MRID 43085901). Thus, based on the following toxicity categories (EFED 2001), methyl bromide (EFED 2001) is considered moderately toxic to bobwhite quail.

- If the LD₅₀ is *less than 10 mg a.i./kg*, then the test substance is *very highly toxic*
- If the LD₅₀ is *10-to-50 mg a.i./kg*, then the test substance is *highly toxic*
- If the LD₅₀ is *51-to-500 mg a.i./kg*, then the test substance is *moderately toxic*.
- If the LD₅₀ is *501-to-2,000 mg a.i./kg*, then the test substance is *slightly toxic*
- If the LD₅₀ is *greater than 2,001 mg a.i./kg*, then the test substance is *practically nontoxic*

Inhalation is the major exposure pathway for birds. However, since no acute inhalation studies in any avian species were identified in the available literature, inhalation toxicity has been estimated (see risk characterization). Overall risk to birds will be assessed using the oral LD₅₀ toxicity value and the LD₅₀/square foot method as a rough risk calculation screen. No chronic exposure studies in any avian species were identified in the available literature.

(iii) Invertebrates

Methyl bromide is used to control a large variety of terrestrial invertebrate species, including nematodes, beetles, termites, weevils, moths and mites. Results of these efficacy studies are summarized in Appendix A4. Given that methyl bromide is used to control a large number target invertebrates, it is likely that non-target terrestrial invertebrates will also be adversely affected by exposure to methyl bromide. It is also likely that the response of non-target species will be highly variable. However, the available data on the effects of methyl bromide in non-target species are more qualitative than quantitative in nature and do not provide sufficient data to allow for quantitative assessment of the risk of exposure of methyl bromide to non-target terrestrial invertebrates.

(D) Toxicity to Other Terrestrial Species

(i) Macrophytes

Methyl bromide has phytotoxic properties and is used as a soil fumigant for weed control. Results of field and greenhouse studies show that methyl bromide is toxic to several types of non-target plants, although the response is highly variable and depends upon experimental conditions. Studies are detailed in Appendix A3. However, in some non-target plant species exposure to methyl bromide results in an improvement in vegetative vigor and yield; these beneficial effects of methyl bromide exposure are presumed to be due to the elimination of pathogenic organisms from soil. Results of several space fumigation studies of stored seeds and grains show that methyl bromide exposure can have significant adverse effects on seed germination, although effects on germination are highly dependent upon exposure conditions, such as temperature and seed moisture content. Results of these soil and space fumigations studies have led to the development of general guidelines regarding the use of methyl bromide to minimize the damage to growing non-target plants and stored seeds. However, these studies do not provide adequate data to quantitatively assess the risk of methyl bromide exposure to germination or vegetative vigor in non-target species. Although the mechanism of toxicity of methyl bromide to plants is not proven, the phytotoxicity of methyl bromide may be due to the excessive accumulation of the bromide ion. However, sufficient data are not available to provide a quantitative risk assessment for exposure of non-target plant species to bromide ion residue in soil. It is also possible that the phytotoxicity of methyl bromide may be, in part, due to the elimination beneficial organisms from soil (MRID 00118842, Lambert et al. 1979). Given the lack of quantitative data on the phytotoxicity of the bromide ion, the risk of exposure of plants to the bromide ion will not be explored.

(ii) Microorganisms

Methyl bromide is used as a soil fumigant for the control of pathogenic fungi and other microorganisms. The efficacy of methyl bromide in target soil microorganisms has been extensively studied, with most data obtained from field and greenhouse studies. Summaries of efficacy studies are provided in Appendix A4. Results of efficacy studies show variability among species regarding sensitivity to methyl bromide; however, given the variation in study protocols and experimental conditions, it is difficult compare study results. Much less information is available on the effects of methyl bromide in non-target microorganisms. Given that methyl bromide is effective in controlling many pathogenic soil microorganisms, it is likely many non-target microorganisms will be affected by methyl bromide exposure. However, the available data on the effects of methyl bromide in non-target species are more qualitative than quantitative in nature and do not provide sufficient data to allow for quantitative assessment of the risk of exposure of methyl bromide to non-target microorganisms.

(E) Toxicity to Aquatic Species

Exposure to aquatic species may occur if ponds or streams are contaminated by run-off from fumigated fields or by accidental spill. Thus, it is possible that under conditions of normal use, methyl bromide could reach concentrations in water that may be toxic to aquatic species. Data are available to allow for a quantitative assessment of risk of methyl bromide exposure in fish, aquatic invertebrates and algae. Toxicity associated with acute exposure of acute exposure is classified according to the following categories (EFED 2001).

- If the LC_{50} is *less than 0.1 ppm a.i.*, then the test substance is *very highly toxic*
- If the LC_{50} is *0.1-to 1.0 ppm a.i.*, then the test substance is *highly toxic*
- If the LC_{50} is *1.0 and up through 10 ppm a.i.*, then the test substance is *moderately toxic*
- If the LC_{50} is *10 and up through 100 ppm a.i.*, then the test substance is *slightly toxic*
- If the LC_{50} is *greater than 100 ppm a.i.*, then the test substance is *practically nontoxic*

In water, the bromide ion is one of the primary degradation products of methyl bromide. Data are available on the acute toxicity of the bromide ion in medaka and guppies, daphnids, and one species of algae (Canton et al. 1983). As demonstrated in Table 16, the bromide ion is much less toxic than methyl bromide to aquatic species. Toxicity endpoints for the bromide ion in aquatic species are summarized in Table 17.

(i) Freshwater Fish, Acute and Chronic

Acute toxicity tests have been conducted in bluegill sunfish, rainbow trout, carp, guppies and medaka. Details of these studies are provided in Appendix A2. For acute exposures, LC_{50} values range from 3.9 mg/L in rainbow trout (MRID 43066701) to 17 mg/L in carp (Segers et al. 1984) and NOAEC values range from 1.4 mg/L (for no mortality) in bluegill sunfish (Dawson et al. 1977) to 1.9 mg/L (for no signs of toxicity) in rainbow trout (MRID 43066701). The results of acute exposure studies indicate that methyl bromide is slightly to moderately toxic to fish, with rainbow trout being the most sensitive species (MRID 43066701).

Studies to assess chronic exposure to methyl bromide have been conducted in guppies and medaka (Webster et al. 1988; Webster and Vos 1994). Details of these studies are provided in Appendix A2. NOAEC values from 1- and 3-month exposures to methyl bromide were of a similar for both species. The lowest NOAEC value reported was 0.1 mg/L for signs of general toxicity following 1-month exposure of guppies.

Acute and chronic exposure tests for the bromide ion (sodium bromide) have been conducted in guppies and medaka (Canton et al. 1983; Webster et al. 1988). Study details are provided in Appendix A5. For acute exposures, the lowest LC_{50} (96 hours) was 16 g Br /L in guppies (Canton et al. 1983). For chronic exposure to bromide ion, the lowest NOAEC (1 month)

VII. AQUATIC AND TERRESTRIAL EXPOSURE AND RISK ASSESSMENT

The risks to terrestrial and aquatic organisms are determined based on risk quotient (RQ) and exceedance of Levels of Concern (LOC) method. This method provides an indication of a chemical's potential to cause an effect in the field from effects observed in laboratory studies, when used as directed. Risk quotients are a ratio of the EEC divided by the corresponding toxicity reference value (TRV):

$$RQ = \frac{\text{Estimated Environmental Concentrations}}{\text{Species Toxicity Value}}$$

The RQ is compared to the level of concern (LOC) to determine the potential for risks. These LOCs, summarized in Tables 18 - 20, are criteria used by OPP to indicate the potential risk to non-target organisms. See Appendix G for additional description of LOCs. For aquatic species, the 24-hour peak concentration in water is used to calculate RQs for acute exposure. For chronic exposure of aquatic species, the averaging time for the EEC and TRV should be as close as possible (e.g., 21 day time-averaged concentration in water and 1-month NOAEC for fish).

Table 18. Risk presumptions for terrestrial animals based on risk quotients (RQ) and levels of concern (LOC).

Risk Presumption	RQ	LOC
Birds		
Acute Risk	EEC/LC ₅₀ or LD ₅₀ /ft ² or LD ₅₀ /day ³	0.5
Acute Restricted Use	EEC/LC ₅₀ or LD ₅₀ /ft ² or LD ₅₀ /day (or LD ₅₀ < 50 mg/kg)	0.2
Acute Endangered Species	EEC/LC ₅₀ or LD ₅₀ /ft ² or LD ₅₀ /day	0.1
Chronic Risk	EEC/NOAEC	1
Wild Mammals		
Acute Risk	EEC/LC ₅₀ or LD ₅₀ /ft ² or LD ₅₀ /day	0.5
Acute Restricted Use	EEC/LC ₅₀ or LD ₅₀ /ft ² or LD ₅₀ /day (or LD ₅₀ < 50 mg/kg)	0.2
Acute Endangered Species	EEC/LC ₅₀ or LD ₅₀ /ft ² or LD ₅₀ /day	0.1
Chronic Risk	EEC/NOAEC	1

¹ abbreviation for Estimated Environmental Concentration (ppm) on avian/mammalian food items

² mg/ft²

³ mg of toxicant consumed/day

LD₅₀ * wt. of bird

LD₅₀ * wt. of bird

reported was 7.8 mg Br⁻/L for adverse reproductive effects in guppies following 124-day exposure.

(ii) Freshwater Invertebrates, Acute and Chronic

The toxicity of methyl bromide in *Daphnia magna* has been assessed following acute exposure. Study details are provided in Appendix A2. An LC₅₀ of 2.6 mg/L, with an NOAEC (for mortality and immobility) of 1.2 mg/L were reported following 48-hour exposure to methyl bromide (MRID 4293290). Based on this study, methyl bromide is classified as moderately toxic to aquatic invertebrates.

The toxicity of the bromide ion to daphnids has been assessed for both acute and chronic exposure (Canton et al. 1983, van Leeuwen et al. 1986). See Appendix A5 for study details. For acute exposure, a 48-hour LC₅₀ value of 11,000 mg Br⁻/L and an NOAEC (for toxicity) of 25 mg Br⁻/L were reported (Canton et al. 1983). For chronic exposure, an NOAEC of 7.8 mg/L, based on reduced reproductive capacity, was reported following a 23-day exposure (Canton et al. 1983).

(iii) Algae and Macrophytes

No information on effects of methyl bromide to aquatic macrophytes was identified in the available literature. Given the adverse effects of methyl bromide to terrestrial plants, it is likely that some aquatic species would also be adversely affected by exposure to methyl bromide. However, due to the lack of data, the assessment of risk of methyl bromide exposure to aquatic plants cannot be made.

Very little information is available on the effects of methyl bromide in algae. Results of a single study provide LC₅₀ values in two species of freshwater green algae (Canton et al. 1980). In *Chlorella pyrenoidosa*, the 48-hour LC₅₀ value was 5.0 mg/L and in *Scenedesmus quadricauda* the 48-hour LC₅₀ value was 3.2 mg/L. The toxicity of the bromide ion has been assessed in a *Scenedesmus quadricauda* (Canton et al. 1983), with a 48-hour LC₅₀ value of 7,800 mg Br⁻/L and a 96-hour LC₅₀ value of 10,000 mg Br⁻/L.

Table 19. Risk presumptions for aquatic animals based on risk quotients (RQ) and levels of concern (LOC).

Risk Presumption	RQ	LOC
Acute Risk	EEC ¹ /LC ₅₀ or EC ₅₀	0.5
Acute Restricted Use	EEC/LC ₅₀ or EC ₅₀	0.1
Acute Endangered Species	EEC/LC ₅₀ or EC ₅₀	0.05
Chronic Risk	EEC/NOAEC	1

¹ EEC = (ppm or ppb) in water

Table 20. Risk presumptions for plants based on risk quotients (RQ) and levels of concern (LOC).

Risk Presumption	RQ	LOC
Terrestrial and Semi-Aquatic Plants		
Acute Risk	EEC ¹ /EC ₂₅	1
Acute Endangered Species	EEC/EC ₀₅ or NOAEC	1
Aquatic Plants		
Acute Risk	EEC ² /EC ₅₀	1
Acute Endangered Species	EEC/EC ₀₅ or NOAEC	1

¹ EEC = lbs ai/A

² EEC = (ppb/ppm) in water

(A) Terrestrial Organisms

Summaries of risk quotients (RQs) for methyl bromide exposure of terrestrial organisms are displayed in Tables E1 and E2 (Appendix E). Available mammalian toxicity data from the Health Effects Division (HED) on methyl bromide (U.S. EPA 2003) is used as a surrogate for wild mammal toxicity. The available toxicity data on the effects of methyl bromide in non-target terrestrial invertebrates and soil microorganisms do not provide adequate quantitative data to determine RQs. However, as summarized in Section 6(B) and Appendix A4, the results of efficacy studies in target organisms show that methyl bromide eradicates many species of terrestrial invertebrates and microorganisms. Thus, adverse effects can be expected for any non-target organisms on the treatment site (e.g., certain digging or burrowing animals or beneficial microorganisms under the treatment tarps). Similarly, due to a lack of quantitative toxicity data, RQs cannot be determined for terrestrial plants. Given that methyl bromide is used to eradicate weeds and is reported to cause damage to some non-target plants (Appendix A3, Appendix A4), methyl bromide exposure resulting from actual labeled use may result in damage to some non-target plant species off-site.

(i) Risk to Mammals

The main route of wild mammal exposure is likely to be from inhalation of methyl bromide off-gassing from treated fields. Mammalian inhalation toxicity data are available. However, EFED does not currently have established LOCs based on inhalation exposure. Nevertheless, an inhalation risk concern for wild mammals has been identified. The analysis based on inhalation toxicity data and exposure data is contained in the Integrated Risk Characterization.

EFED has used the established LD_{50} /square foot risk assessment method for mammals (and birds) as a risk calculation screen. This method is considered to cover all routes of exposure, although it uses an acute oral toxicity value. It is typically used for granular and similar products, but it is considered acceptable for use as a screen for methyl bromide. Uncertainties of the method, in general, include 1) non-oral routes of exposure may be either more or less hazardous than the oral route, and 2) an organism would not typically take up all the toxicant from any given square foot, and the amount of toxicant in this unit of area may be more or less than that which an organism receives overall as a dose. For evaluating exposure to a highly volatile chemical applied below ground, there is added uncertainty since all the chemical applied is not available at the surface at any one time, for example. Its value for the present assessment is as a preliminary screen to confirm whether a refined route-specific (e.g., inhalation) analysis is appropriate.

Using the 400 lb ai/A rate used in calculating aquatic EECs (see previous Water Resource Assessment), there would be 4165 mg methyl bromide/square foot (given 43,560 square feet/A and 453,590 mg/lb). This exposure amount is divided by the product of acute oral LD_{50} for mammals (86 mg/kg) and body weight of mammal (in kg) to calculate risk quotients. Three mammal body weights are assessed: 15g, 35g, and 1000g. The resulting risk quotients for these

three sizes of mammals are 3,229, 1,384, and 48, respectively (Table E1). These far exceed the acute risk LOC of 0.5, as well as the acute restricted use LOC of 0.2 and the acute endangered species LOC of 0.1. Thus, this preliminary screen indicates a potential for concern for risk to wild mammals. See the Integrated Risk Characterization for the more refined assessment of risk based on inhalation exposure.

(ii) Risk to Birds

As with mammals, the main route of exposure of birds is likely to be from inhalation of methyl bromide off-gassing from treated fields. As with mammals, EFED does not currently have established LOCs based on inhalation exposure. Nevertheless, an inhalation risk concern for birds has been identified. The analysis based on estimated avian inhalation toxicity data and exposure data is contained in the Integrated Risk Characterization.

EFED has used the established LD_{50} /square foot method for birds as a rough risk calculation screen (see uncertainty discussion above), using the same 4165 mg methyl bromide/square foot exposure amount used above for mammals. This exposure amount is divided by the product of acute oral LD_{50} for birds of 73 mg/kg (MRID 43085901) and body weight of birds (in kg) to calculate risk quotients. Three avian body weights are assessed: 0.01 kg, 0.4 kg, and 4 kg. This range of weights was chosen to illustrate the effect of bird size on risk. The weight of 0.01 kg is representative of the body weight of several species of small birds, 0.4 kg represents the weight of a quail, and 4 kg represents the weight of a large bird, such as a Canada goose (U.S. EPA/ORD (1993)). The resulting risk quotients are 5705, 143, and 14, respectively (Table E2). These far exceed the acute risk LOC of 0.5, as well as the acute restricted use LOC of 0.2 and the acute endangered species LOC of 0.1. Thus, this preliminary screen indicates a potential for concern for risk to wild mammals. See the Integrated Risk Characterization for the more refined assessment of risk based on inhalation exposure.

Ecotoxicity data for terrestrial animals on an acute basis is limited by the number of species tested. Variability in toxicity to chemicals across species can, at times, be quite high. Additionally, using only one bird and one mammal species to represent all terrestrial animals may result in the underestimation of risks for some particularly sensitive animal while overestimating the risks of others. In addition, use of laboratory rats as surrogates for wild mammals has inherent uncertainties because laboratory mammals are generally bred to minimize genetic variability and to be sensitive to chemical exposures – i.e., likely to exhibit responses at lower doses. In these cases, toxicity may be overstated. The LD_{50} /sq. ft. method is a rough screen only. It essentially assumes that all the chemical applied to a square foot could be available at one time via all exposure routes combined and compares that to available acute oral toxicity data. For methyl bromide, the gas will either break down underground to its degradates (such as the bromide ion) or gradually off-gas at the surface.

(B) Risk to Aquatic Organisms

(i) Methyl Bromide

Risk quotients for acute and chronic exposure of aquatic organisms to methyl bromide are summarized in Tables E5 and E6, Appendix E. As described in Section 5(A), estimated environmental concentrations (EEC) of methyl bromide in surface waters were calculated for the application rate of 400 lb/acre using PRZM/EXAMS for four PRZM field scenarios: California tomatoes, California grapes, Florida strawberries, and North Carolina tobacco. A Mississippi pond scenario was used to determine estimated environmental concentrations (EEC) for ecological risk assessment. For all aquatic organisms, calculation of RQs for acute exposures was based on EECs for 24-hour peak concentrations. Results of the 1-in-10 year probabilities are summarized in Table 12 and the full set of EECs are given in Appendix C. The highest EECs were observed for the California tomatoes and Florida strawberries scenarios.

The toxicity endpoints for aquatic species are summarized in Table 14. The toxicity data for acute exposures indicate that methyl bromide is slightly to moderately toxic to all aquatic organisms tested. The lowest acute LC₅₀ values reported for fish, aquatic invertebrates and algae were similar, ranging from 2.2 ppm in algae to 3.9 ppm in rainbow trout.

As shown in Tables E5 and E6, RQs for acute exposure range from approximately 0.012 (North Carolina tobacco) for fish to approximately 0.077 for algae (Florida strawberries). Thus, none of the exposure scenarios result in RQs that meet or exceed the acute (LOC, 0.5) or restricted use (LOC, 0.1) levels of concern for freshwater fish or invertebrates, or the acute (LOC, 1) level of concern for aquatic plants.

Regarding the level of concern for endangered species (LOC, 0.05), risk quotients exceed the level of concern for aquatic invertebrates for California tomatoes (RQ, 0.062) and Florida strawberries (RQ, 0.066). Thus, based on the modeled exposure scenarios, there appears to be a potential risk of acute toxicity to endangered/threatened aquatic invertebrates that may be exposed. However, as described earlier in the Water Resources Assessment (Section V), there is an uncertainty in estimating methyl bromide exposure due to post-application tarping of the treated area and its relation to chemical loading through runoff in water bodies. Given the low levels of exceedence (RQs of 0.06 to 0.07), the potential effect of tarping might reduce the exposures, which in turn might reduce the RQs below the LOC. Additional data on the marine/estuarine mollusk test species should improve the level of certainty with this assessment, as this test species may be more representative of endangered freshwater mussels than the freshwater *Daphnia*.

Risk quotients for fish approach the endangered species level of concern (0.05) for California tomatoes (RQ, 0.041) and Florida strawberries (RQ, 0.044). Thus, even a slight increase in the application rate over that modeled for these sites would push the RQ over the LOC.

For chronic exposure of fish, the RQs for all four exposure scenarios are below the level of concern (LOC, 1) for chronic exposures for freshwater fish. The highest risk quotient for chronic exposure of fish (California tomatoes) is 0.35. Chronic toxicity data for other aquatic species are not available; thus, the risk of chronic exposure to methyl bromide in other aquatic organisms was not assessed.

(ii) Bromide Ion

In water, the bromide ion is one of the primary degradation products of methyl bromide. Since the bromide ion may persist longer in water than methyl bromide, potentially resulting in the accumulation of the bromide ion in water, the risk of aquatic exposures to the bromide ion was considered. As shown in Table 16, relative to methyl bromide, the bromide ion is far less toxic to aquatic organisms, by factors ranging from approximately 1,400 to 34,000. The most sensitive measures of toxicity data for the bromide are summarized in Table 17. For acute exposures to bromide ion, LC_{50} values range from 780 ppm in algae (96-hour exposure) to 16,000 ppm in guppies (96-hour exposure). However, aquatic organisms appear far more sensitive to chronic than acute exposure to bromide ion, with NOAECs of 7.8 ppm for adverse effects on reproduction in both guppies and *Daphnia magna*.

Monitoring data are available for surface waters associated with areas of methyl bromide use (Table 13), with bromide ion concentrations ranging from 0.061 ppm (location not specified) (USGS NAWQA 2004) to 72 ppm in drainage water nearby a greenhouse fumigated with methyl bromide (WHO 1995). Although insufficient data are available on chronic EECs for the bromide ion to calculate a chronic RQ, the levels of bromide ion in surface water based on this monitoring exceed the chronic toxicity values observed for fish and aquatic invertebrates (7.8 ppm, see Table 15). Thus, there is a potential for chronic toxicity for fish and aquatic invertebrates exposed to bromide ion residues in water. However, bromide concentrations in the monitoring data are not associated with a soil fumigation of methyl bromide; thus, it is unclear how these concentrations would correspond to water contaminated with methyl bromide runoff from a nearby field or to exposures scenarios for aquatic receptors. Therefore, Tier I GENEEC model was used in estimating bromide ion EECs. The maximum chronic concentration for the modeled pond was slightly below the chronic endpoints based on open literature data. Guideline chronic ecological effects data on the bromide ion are needed for a complete assessment and to reduce uncertainty.

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Appendix A1: Effects Data: Toxicity of Methyl Bromide to Terrestrial Animals (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Animal	Dose/Exposure	Response	Reference
MAMMALS			
rabbits	Teratology study	No adverse maternal or fetal effects observed in the 20 or 40 ppm exposure groups.	MRID 41580401 (Breslin et al. 1990)
	Inhalation exposure to methyl bromide vapor concentrations of 0, 20, 40, or 80 ppm for 6 hrs/day on days 7-19 of gestation. As noted in the HED HIARC report (U.S. EPA 2003), the 40 ppm exposure is equivalent to 15 mg/kg/day and the 80 ppm exposure is equivalent to 28 mg/kg/day.	In the 80 ppm exposure group, clinical signs of toxicity observed (neurotoxicity, decreased body weight). Developmental effects observed in fetus (agenesis of gallbladder, increased incidence of fused sternebrae) NOAEL (maternal and fetal toxicity) = 40 ppm The NOAEL of 40 ppm (14 mg/kg/day) was used to derive the acute RfD	acceptable/guideline
rats	methyl bromide vapor for 6 hours at concentrations of 0, 30, 100, and 350 ppm	No mortalities in any exposure group. Pathological examination conducted 15 days after exposure.	MRID 42793601 (Driscoll and Hurley 1993)
	According to HED HIARC Report (U.S. EPA 2003) exposure equivalent to the following daily doses – males: 0, 27, 90, and 314 mg/kg/day; females: 0, 30, 101, and 354 mg/kg/day	Clinical signs of toxicity observed only in the 350 ppm exposure group: decrease in arousal, increases parasympathetic nervous system activity. Symptoms resolved at end of exposure period. No exposure-related gross or microscopic findings in any treatment group. NOAEL (for clinical signs of toxicity) = 100 ppm (equivalent to 90 mg/kg/day) LOAEL (for clinical signs of toxicity) = 350 ppm (equivalent to 314 mg./kg/day)	Acceptable/guideline

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Animal	Dose/Exposure	Response	Reference
dogs	<p>Inhalation exposure to 0, 5, 10 (increased to 150 during last 2 weeks of exposure), 25, 50, 100 and 150 ppm methyl bromide vapor for 7 hours/day, 5 days/week for 5, 6, or 7 weeks. Actual concentrations measured were 0, 5.3, 11.0/158.0, 26.0, 53.1 or 102.7 ppm.</p> <p>According to the HED HIARC report (U.S. EPA 2003), these exposure levels are equivalent to 1.43, 2.97/42.7, 7.02, 14.3, and 27.7 mg/kg/day</p>	<p>No treatment-related deaths. No macroscopic finding upon necropsy in any exposure group. Microscopic changes in the CNS in the 150 exposure group.</p> <p>Clinical effects (signs of neurotoxicity) appeared to be cumulative based on exposure duration, with NOAEL and LOAEL values decreasing with increasing exposure periods.</p> <p>For 5-week exposure period NOAEL = 26 ppm LOAEL = 53.1 ppm</p> <p>For 6-week exposure period NOAEL = 5.3 ppm LOAEL = 10 ppm</p> <p>For 7-week exposure period NOAEL < 5.3 ppm LOAEL = 5.3 ppm (equivalent to 1.43 mg/kg/day) Decreased responsiveness in 2/8 dogs (both females) in the 5.3 ppm group after 7 weeks of exposure.</p>	<p>MRID 43386802 (Newton 1994)</p> <p>Acceptable/non-guideline</p>

Appendix A1: Effects Data: Toxicity of Methyl Bromide to Terrestrial Animals (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Animal	Dose/Exposure	Response	Reference
albino rats	methyl bromide liquid (in corn oil) and microencapsulated methyl bromide (in corn oil). Both administered at doses of 80, 120, and 160 mg a.i./kg by gavage	<p><u>methyl bromide liquid</u> females: LD₅₀ = 86 mg a.i./kg (95% confidence limits of 77-95 mg/kg)</p> <p>males: LD₅₀ = >120 but <160 mg a.i./kg</p> <p>combined males and females: LD₅₀ = 104 mg a.i./kg (95% confidence limits of 83-120 mg/kg)</p> <p><u>microencapsulated methyl bromide:</u> females: LD₅₀ = 105 mg a.i./kg (95% confidence limits of 95-116 mg/kg)</p> <p>males: LD₅₀ = 159 mg a.i./kg (95% confidence limits of 131-192 mg/kg)</p> <p>combined males and females: LD₅₀ = 133 mg a.i./kg (confidence limits of 106-167 mg/kg)</p> <p>Authors state that no remarkable quantitative or qualitative differences were observed between the two liquid and microencapsulated methyl bromide.</p> <p>NOTE: In an preliminary confirmatory phase of the study, the LD₅₀ for liquid methyl bromide was 122 mg a.i./kg (males and females combined)</p>	MRID 43510301 (Kiplinger 1994)

Appendix A1: Effects Data: Toxicity of Methyl Bromide to Terrestrial Animals (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Animal	Dose/Exposure	Response	Reference
rats	<p>dietary exposure to 0, 0.5, 2.5, 50, and 250 ppm for up to 104 weeks.</p> <p>According to the HED HIARC report (U.S. EPA 2003), concentration in food equivalent to the following daily doses – males: 0, 0.02, 0.11, 2.20, 11.10 mg/kg/day; females: 0, 0.03, 0.15, 2.92, and 15.10 mg/kg/day</p>	<p>No treatment-related mortalities. No treatment-related increase in tumor incidence.</p> <p>Clinical signs of toxicity (decreased body weight, decreased weight gain and decreased food consumption) observed in the 250 ppm exposure group.</p> <p>NOAEL = 50 ppm (equivalent to 2.2 mg/kg/day in males and 2.92 mg/kg/day in females)</p> <p>LOAEL = 250 ppm (equivalent to 11.1 mg/kg/day in males and 15.1 mg/kg/day in females)</p> <p>The NOAEL of 2.2 mg./kg/day was used to derive the RfD fro chronic oral exposure</p>	<p>MRID 44462501 (Mertens 1997)</p> <p>acceptable/ guideline</p>
rats (male Sprague-Dawley)	<p>4-hours inhalation exposure to 502, 622, 667, 799, 896 ppm methyl bromide.</p> <p>According to the HED HIARC Report (U.S. EPA 2003), 780 ppm is equivalent to 3.03 mg/L)</p>	<p>LC₅₀ values calculated from mortality 1 week after exposure.</p> <p>LC₅₀ = 780 ppm (95% Confidence Limit: 760-810 ppm)</p>	<p>Kato et al. 1986</p>

Appendix A1: Effects Data: Toxicity of Methyl Bromide to Terrestrial Animals (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Animal	Dose/Exposure	Response	Reference
BIRDS			
bobwhite quail (21 weeks)	Acute oral toxicity study.	100% mortality at doses ≥ 125 mg/kg. First mortality observed within 2 hours after dose.	MRID 43085901 (Campbell and Beavers 1994)
5M/5F per test group	Methyl bromide(100% a.i.) administered by gavage at doses of 0, 31.3, 62.5, 125, 250, 500, and 1000 mg/kg.	$LD_{50} = 73$ mg a.i./kg [95% Conf. Limit 62.5 to 125 mg/kg]	Core Study ^a
	7-day observation period	NOAEC (mortality) = 31.3 mg/kg Clinical signs of toxicity (loss of coordination, limb weakness, lethargy, loss of righting reflex, shallow respiration) observed in lowest dose group. Dose-related decrease in body weight.	
MICROORGANISMS			
Mycorrhizae (symbiotic soil fungus)	Field study. 1 pound methyl bromide applied under tarp to plots (size not specified) of Virginia and slash pines seedlings	Methyl bromide treatment completely suppressed growth of Mycorrhizae on pine roots Seedlings in methyl bromide plots showed increased growth compared to control plots. Proposed that growth of seedling improved due to elimination of pathogenic organisms.	MRID 00031105 (Hacskayko and Palmer 1957)
<i>Nitrosomonas europaea</i> (soil nitrifying bacteria)	Laboratory study. Cells exposed <i>in vitro</i> to 0.11, 0.22, and 0.44 mM methyl bromide for 24 hours	At 0.44 mM concentration, 90% of NH_3 -dependent O_2 uptake activity and the NO_2^- - producing activity was lost. When media was refreshed, activities returned to control levels within 48-60 hours.	Duddleston et al. 2000
methanogens (archaeobacteria found in anaerobic environments – species not specified)	<i>In vitro</i> study. Exposure period and concentration range not specified	IC_{50} value = 0.04 mM	Trevizon and Nirmalakjandan 1999

Appendix A1: Effects Data: Toxicity of Methyl Bromide to Terrestrial Animals (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Animal	Dose/Exposure	Response	Reference
various soil bacteria	Greenhouse study. Soil samples analyzed 7 months after methyl bromide application (formulation and application technique not specified). Soil samples from 2 depths: 0-30 cm and 30-60 cm	Rapid re-colonization of ammonifying bacteria 0-30cm samples: total mesophile bacteria, aerobic nitrogen-fixing, ammonifying, ammonia-oxidizing, and nitrite-oxidizing bacteria counts higher than in untreated control plots. 30-60 cm samples: aerobic nitrogen-fixing, and ammonifying counts higher than untreated control plots	Turtura et al. 1988
Soil bacteria	core soil samples fumigated in the laboratory with methyl bromide (48 g/m ³). Samples then returned to field and monitored at 1, 5, 12, 26, 54, 110, and 166 days	Total microbial mass recovered rapidly, especially in dry soils. Mineral nitrogen greater in treated sites than in non-treated sites (most likely due to mineralization of substances liberated from killed organisms) Overall, bacterial counts were comparable to untreated soils. Fungal populations were markedly lower than controls, but by day 12, populations had recovered. Protozoan populations were totally eliminated initially. Populations recovered to control levels by 166 days after treatment.	Yeates et al. 1991

a Core means satisfies guidelines; supplemental means study is scientifically sound, but does not satisfy guidelines.

Appendix A2: Effects Data: Toxicity of Methyl Bromide to Aquatic Species (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Animal	Dose/Exposure	Response	Reference
Fish			
rainbow trout	96-hour static acute toxicity test at methyl bromide (100% a.i.) concentrations of 0, 1.3, 1.9, 2.9, 4.6, and 7.7 mg a.i./L (measured concentrations). Mortality and clinical signs of toxicity assessed at 14, 24, 48, 72, and 96 hours.	At concentrations of 7.7 mg/L, 100% mortality observed. 85% mortality at 4.6 mg/L. Clinical signs of toxicity included lethargy and loss of equilibrium. LC₅₀ (96-hr) = 3.9 mg a.i./L [95% confidence limits of 2.9 and 4.6 mg/L] NOAEC (for mortality) = 2.9 mg a.i./L NOAEC (for clinical signs of toxicity) = 1.9 mg a.i./L	MRID 43066701 (Drottar and Swigert 1993b) Supplemental study ^a
medaka (<i>Oryzias latipes</i>) and guppy (<i>Poecilia reticulata</i>)	methyl bromide (concentration range not specified)	medaka: 48-hour LC₅₀ = 1.6 mg/L 72-hour LC₅₀ = 0.9 mg/L 96-hour LC₅₀ = 0.7 mg/L guppy: 24-hour LC₅₀ = 2.2 mg/L 48-hour LC₅₀ = 1.7 mg/L 72-hour LC₅₀ = 0.8 mg/L 96-hour LC₅₀ = 0.8 mg/L	Canton et al. 1980
bluegill sunfish (freshwater) and tidewater silversides (saltwater)	<u>Bluegills</u> : exposure to methyl bromide concentrations ranging from 1.4, 7, 11, and 14 ppm for bluegills <u>Silversides</u> : exposure to 7, 11, and 14 ppm for silversides. All exposures under static conditions for up to 96 hours	<u>bluegill sunfish</u> : LC₅₀ (96-hr) = 11 ppm At 48 hours, 100% mortality observed in 14 ppm group. At 96 hours, 10% mortality observed in 7 ppm group NOAEC (96-hr mortality) = 1.4 ppm <u>tidewater silversides</u> : LC₅₀ (96 hr) = 12 ppm At 24 hours, 100% mortality observed in 14 ppm group. At 96 hours, 20% mortality observed in 7 ppm group (lowest dose tested)	Dawson et al. 1977

Appendix A2: Effects Data: Toxicity of Methyl Bromide to Aquatic Species (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Animal	Dose/Exposure	Response	Reference
carp (<i>Cyprinus carpio</i>)	4-hour exposure to methyl bromide concentrations of 0, 9.3, 13.9, 18.5, 28.0, and 36.0 mg/L. Fish evaluated 48 hours after exposure.	<p>LC₅₀ (4-hr) = 17 mg/L.</p> <p>In the 36.0 mg/L group, all fish died during the 4-hour exposure. 12.5% mortality observed at 9.3 mg/L (lowest dose tested and 0% mortality at 13.9 mg/L.</p> <p>Most pronounced sign of toxicity was morphological damage to gill epithelium (indicative of alkylation of cell membranes). Specific changes include swelling of lymphatic space, vacuolization of epithelial cells and invasion of leukocytes. Likely cause of death was suffocation.</p>	Segers et al. 1984
medaka (<i>Oryzias latipes</i>) and guppy (<i>Poecilia reticulata</i>)	methyl bromide for 1-3 months. Concentration range not specified.	<p><u>guppy</u>: irritation of superficial epithelium. No significant histopathology observed.</p> <p>For 1 month exposure, NOAEC for general toxicity (not specified) = 0.1 mg/L</p> <p><u>medaka</u>: irritation of superficial epithelium. No significant histopathology observed.</p> <p>For 1 month exposure, NOAEC for general toxicity (not specified) = 0.56 mg/L</p> <p>For 3 month exposure, NOAEC for general toxicity (not specified) = 0.18 mg/L</p>	Webster and Vos 1994

Appendix A2: Effects Data: Toxicity of Methyl Bromide to Aquatic Species (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Animal	Dose/Exposure	Response	Reference
guppy (<i>Poecilia reticulata</i>) and medaka (<i>Oryzias latipes</i>)	<p><u>guppies</u>: Acute exposure to methyl bromide for 4 hours (0.56, 1.0, 1.8 mg/L). Chronic exposure to methyl bromide (0.032 - 3.2 mg/L) for 1 and 3 months.</p> <p><u>medaka</u> (embryos): Acute exposure to methyl bromide for 4 hours (0.56, 1.0, 1.8 mg/L). Chronic exposure to methyl bromide (0.1 - 3.2 mg/L) for 3 weeks and 3 months.</p> <p>For all exposures, methyl bromide was technical grade.</p>	<p>Acute Exposure: Dose-related degenerative and regenerative changes to superficial epithelia of gills and oral mucosa in both species. <u>guppies</u>: Reduced activity in all exposure groups. Limited mortality (not specified) in 1.0 and 1.8 mg/L groups. <u>medaka</u>: Reduced activity in all exposure groups. Limited mortality (not specified) in 1.0 and 1.8 mg/L groups.</p> <p>Chronic Exposure (1 and 3 months): <u>guppies</u>: In 3.2 mg/L group, all fish died within 3 days. In 1.0 mg/L group, all fish died within 3 weeks. NOAEC (lethality) (exposure period not specified) = 0.32 mg/L; NOAEC (toxicity) (exposure period not specified) = 0.1 mg/L. <u>medaka</u>: All embryos in the 1.8 and 3.2 mg/L groups and most in the 1.0 mg/L group died before hatching. 3-month NOAEC (lethality) = 0.32 mg/L; 1-month NOAEC (toxicity) = 0.56 mg/L; 3-month NOAEC (toxicity) = 0.32 mg/L</p>	<p>Webster et al. 1988</p> <p>Some results also reported in Webster and Vos 1994</p>
Aquatic Invertebrates			
<i>Daphnia magna</i>	<p>48-hour static exposure at methyl bromide (100%) concentrations of 0, 1.2, 2.2, 3.5, 5.8, and 9.8 a.i. mg/L (measured concentrations).</p> <p>Mobility and mortality assessed at 24 and 48 hours</p>	<p>At concentrations ≥ 3.5 mg/L, 100% mortality was observed</p> <p>LC₅₀ (48-hr) = 2.6 mg a.i./L [95% Confidence limits of 2.2 and 3.5 mg/L]</p> <p>NOAEC (mortality and immobility) = 1.2 mg a.i./L</p>	<p>MRID 42932901 (Drottar and Swigert 1993a)</p> <p>Core Study ^a</p>
<i>Daphnia magna</i>	methyl bromide (concentration range not specified)	LC₅₀ (48-hr) = 2.2 mg a.i./L	Canton et al. 1980
Algae			

Appendix A2: Effects Data: Toxicity of Methyl Bromide to Aquatic Species (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Animal	Dose/Exposure	Response	Reference
Green algae (<i>Chlorella</i> <i>pyrenoidosa</i> and <i>Scenedesmus</i> <i>quadricauda</i>)	methyl bromide (concentration range not specified)	<i>Chlorella pyrenoidosa</i> 24-hour LC ₅₀ = 6.7 mg/L 48-hour LC ₅₀ = 5.0 mg/L <i>Scenedesmus quadricauda</i> 24-hour LC ₅₀ = 2.2 mg/L 48-hour LC ₅₀ = 3.2 mg/L	Canton et al. 1980

a Core means satisfies guidelines; supplemental means study is scientifically sound, but does not satisfy guidelines.

Appendix A3: Effects Data: Toxicity of Methyl Bromide to Terrestrial Plants (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Plant Species	Dose/Exposure	Response	Reference
citrus trees: Hamlin orange, Tangerine and Valencia orange planted on different root stocks	Field study 1 pound methyl bromide was applied to plots (15 ft x 15 ft) by probe injector	No evidence of phytotoxicity up to 3 years after plantings.	MRID 00013036 (O'Bannon 1972) Data also reported in MRID 00034654 (Bistline and O'Bannon 1972)
citrus trees	Field study. Methyl bromide (98%, plus 2% chloropicrin) applied at rate of 625 lb/acre and tarped	Trees observed for damage for from methyl bromide to determine if damage was related to bromide levels in leaves. No relationship between leaf bromide levels and damage was observed	MRID 00013162 (Great Lakes Chemical Corporation 1971)

Appendix A3: Effects Data: Toxicity of Methyl Bromide to Terrestrial Plants (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Plant Species	Dose/Exposure	Response	Reference
several plant varieties	General review of non-target plant susceptibility. No data provided in this paper.	In general, symptoms of methyl bromide toxicity are first noticed on growing tips and roots <u>most greenhouse plants</u> : safe at application rate of 1 lb/1000 ft ³ <u>non-dormant roses</u> : susceptible to injury at application rate > 0.25 lb/1000 ft ³ <u>ornamental conifers</u> : susceptible during spring growth, but not in winter <u>peach trees</u> : safe at 2 lb/1000 ft ³ <u>strawberry plants</u> : tolerate application rates up to 3 lb/1000 ft ³ , exposure at higher rates to non-dormant plants can be severe <u>camellias</u> : tolerate 3 lb/1000 ft ³ , but toxicity increased by increased light and temperature; decreased by transpiration rate of plants <u>apple trees</u> : some varieties damaged at 2.5 lb/1000 ft ³ <u>legume and cereal seeds</u> : germination unaffected at concentrations up to 160 mg/L <u>fruits</u> : at 2.5 lb/1000 ft ³ , ripening of tomatoes and papaya; damage to oranges and apples at 2.4 lb/1000 ft ³ ; most fruits damaged by 3 lb/1000 ft ³	MRID 00069661) Reddick Fumigants 1974?) Same information reported in MRID 00069665 (Reddick Fumigants 1974?)

Appendix A3: Effects Data: Toxicity of Methyl Bromide to Terrestrial Plants (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Plant Species	Dose/Exposure	Response	Reference
various plants	Review	<p>Breakdown of methyl bromide in soil results in liberation of inorganic bromide. Certain plants (tomato, orange, carrot, lima bean, lemon, tobacco, beet, snap bean, cabbage, carnation, wheat, lettuce and radish) accumulate inorganic bromide in foliage and other parts of the plants.</p> <p>Normal concentration of Br in plant foliage are highly variable and generally $<50 \mu\text{g/g}$ dried material. Following treatment with methyl bromide, concentration can increase to 35 mg/g dried tissue.</p> <p>Phytotoxic effects of methyl bromide may be attributed to methyl bromide, inorganic bromide, or indirect action of methyl bromide on soil microflora, soil composition or structure.</p> <p>Response to plants highly variable depending on conditions and plant type.</p> <p>Carnation appears to be highly sensitive to bromide in soil, and shows damage at soil concentrations of $5 \mu\text{g/g}$ soil. Although lettuce accumulates high concentrations of bromide, it is highly resistant to toxicity.</p>	MRID 00118842 (Maw and Kempton 1973)

Appendix A3: Effects Data: Toxicity of Methyl Bromide to Terrestrial Plants (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Plant Species	Dose/Exposure	Response	Reference
beans (<i>Phaseolus vulgaris</i>)	Fumigation study with methyl bromide (concentration of 20 mL/m ³)	methyl bromide decreased germination and vigor. Effects increased with increasing storage time after treatment. Seeds with higher moisture content were more susceptible to treatment	Araujo et al. 1985
cineraria (daisy like flower), poinsettia, tomato, spruce seedlings	Greenhouse study on actively growing plants. Fumigation chamber size, 50 ft ³ . Methyl bromide applied at 1521 lb/1000 ft ² for 2 hours, plants exposed to vapor [authors note that this does gives 100% control over red spider infestations]. 90% relative humidity.	<u>Tomato seedlings</u> : wilting and burning of leaves. 2 weeks after exposure, plants were stunted. Respiration rate of plants decreased approximately 50%. Ammonia content of leaves decreased significantly within 4 hours after exposure, but returned to normal within 162 hours after exposure. <u>Spruce</u> : no obvious effects until 7- 10 weeks after exposure, then leaves started to drop. Respiration rate of plants decreased approximately 50% <u>Transpiration studies</u> : methyl bromide exposure had no affect on transpiration rate in tomato, cineraria or poinsettia. Effects of methyl bromide appear to be related, in part, to the ability of water absorption by roots (plants with roots sealed in wax prior to fumigation did not wilt). Soil O ₂ content decreased by ~80% following methyl bromide application; damage may be the result of decrease in soil O ₂ content.	Beames and Butterfield (no date)

Appendix A3: Effects Data: Toxicity of Methyl Bromide to Terrestrial Plants (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Plant Species	Dose/Exposure	Response	Reference
Several types of grain seeds: wheat (Piko), wheat (Atle), oats (Star), oats (Blenda) barley (Procter), barley (Herta), rye (Winter), and maize (W268)	Germination study. Fumigation of seeds with methyl bromide (at one of three doses: time × concentration products of 0, 600, and 1200 mg•hr/L).	Germination tested at 6 months, 3 years and 6 years after fumigation at seed moisture contents of 8, 11, 14, and 18%. At lowest moisture content, good survival of all seeds was observed. In control and methyl bromide treated seeds, germinative capacity decreased with increasing seed moisture content. Effects of methyl bromide more pronounced at higher seed moisture content.	Blackith and Lubatti 1965
Strawberry seedlings	Field study. Pre-plant soil fumigation with methyl bromide (67%)-chloropicrin (33%) formulation, applied at 392 kg/ha (not specified if a.i. or formulation)	No affect of methyl bromide on plant mortality. Plant diameter and fruit yield was higher in methyl bromide treated plants compared to untreated plants.	Fort and Shaw 1996
barley (several varieties)	Germination study. Fumigation of seeds (200 mg/hr/L)	Effects of methyl bromide on seed germination and germinative capacity can depend of plant variety, seeds moisture content, and methyl bromide dose. Damage to plants following fumigation of seeds include albinism and stunted growth. Residual bromide residue content was not a reliable indicator of the extent of methyl bromide exposure	Hanson et al. 1987

Appendix A3: Effects Data: Toxicity of Methyl Bromide to Terrestrial Plants (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Plant Species	Dose/Exposure	Response	Reference
Conifer seeds (several species: scotch pine, mugo pine, Norway spruce, White spruce)	Germination study. Fumigation of seeds at 3 lb methyl bromide/1000 ft ³ for 2.5 hours at a temperature of 10-79°F. Range of seed moisture content (5, 10, and 15%).	<u>Scotch pine</u> : reduced germination at 10 and 15% seed moisture content.	Jones and Havel 1968
		<u>Mugo pine</u> : germination decreased with increasing seed moisture content.	
		<u>Norway spruce</u> : germination decreased with increasing seed moisture content. Most sensitive of species tested.	
		<u>Norway spruce</u> : reduced germination at 10 and 15% seed moisture content.	
		<u>White spruce</u> : reduced germination at 10 and 15% seed moisture content.	
carnation plants	Greenhouse study. Pre-plant soil fumigation with methyl bromide (not specified if 100%) at rates of 0.5, 1.0, and 1.5, lb/100 ft ² (24, 49, and 73 g/m ²). Carnation cuttings planted 14 days after fumigation.	24-hour aeration following fumigation improves germination.	Kempton and Maw 1974
		Injury became evident 5 weeks after planting. Dose-related effects for plant injury, flower yield and plant death. Surviving plants were stunted and flower production was reduced. Damage to plants was decreased if plots were flooded with water or peat was incorporated into the soil. Plant survival and flower yield were inversely proportional to inorganic bromide concentration of soil. Injury to plants was observed with soil bromide concentrations of 5 µg/g soil. Bromide content of injured plants greater than in healthy plants.	

Appendix A3: Effects Data: Toxicity of Methyl Bromide to Terrestrial Plants (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Plant Species	Dose/Exposure	Response	Reference
peach seedlings	Field study. Prior to planting, formulation containing 67% methyl bromide-33% chloropicrin, 275 kg/ha (not specified if this is a.i. or formulation) was applied	Severe stunting occurred in random areas of the treated field. Damage was associated with deficiencies in soil content of P, Cu, and Zn. In these areas, root colonization of mycorrhizal was poor. Appears that stunting is secondary to elimination of mycorrhizal fungi.	Lambert et al. 1979
Strawberry plants	Field study. Pre-plant soil fumigation with methyl bromide (67%)-chloropicrin (33%) formulation, applied by soil injection at 392 kg/ha (not specified if a.i. or formulation)	No change in plant mortality for methyl bromide treated plants compared to untreated controls. Leaf dry mass, crown dry mass, and root dry mass greater in methyl bromide treated plots than in untreated plots. No difference between methyl bromide and controls for shoot:root dry mass.	Larson and Shaw 1996
peanuts	Germination tests on peanuts fumigated in flasks with methyl bromide (formulation not specified) at concentrations ranging from 17.3 to 50.9 mg/L for 24 hours	Methyl bromide at concentrations of 17.3 and 24.5 mg/L did not adversely affect germination. At doses > 24.5 mg/L, dose dependent decrease in germination observed.	Minton and Gillenwater 1973

Appendix A3: Effects Data: Toxicity of Methyl Bromide to Terrestrial Plants (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Plant Species	Dose/Exposure	Response	Reference
Onion seeds (several varieties)	Laboratory Germination study (conditions mimicked cool spring conditions). Technical grade methyl bromide or formulation containing 98% methyl bromide and 2% chloropicrin. Seeds fumigated at 1000 and 2000 mg/hr/L.	Dose-dependent decrease in germination observed. Germination also decreased with decreasing temperature. The methyl bromide chloropicrin formulation had a tendency to have a greater decrease in germination compared to methyl bromide alone (not statistically significant). Differences observed between varieties. Some loss of vigor observed at the higher treatment levels (not quantified)	Powell 1975
rice and corn seeds	Technical grade methyl bromide (99.5% a.i.). <u>Germination studies:</u> Fumigation in sealed flasks at 25, 30, and 35°C for 3 and 5 days. For rice seeds, concentrations of 0, 1, 2, 3, 4, and 5 mg/L in sealed flask. For corn seeds, concentrations of 0, 3, 10, 15, 20, and 25 mg/L. <u>Sorption studies:</u> fumigation at 35°C for 5 days. For rice seeds, 1, 3, and 5 mg/L methyl bromide. For corn seeds, 5, 10, and 20 mg/L.	<u>Germination studies:</u> Corn seeds appear more tolerant than rice seeds. Rice seeds show dose-dependent decrease in germination, with further decreases at higher temperatures. Decreased germination also observed with higher moisture content of seeds. Corn seeds show a similar pattern, but decreased in methyl bromide-induced decreased germination was less than observed in rice seeds. <u>Sorption studies:</u> Rice seeds sorbed more methyl bromide than corn seeds. Sorption increased with increasing moisture content of seeds. Increases in sorption also observed with increasing temperature.	Sittisaung and Nakaita 1985

Appendix A3: Effects Data: Toxicity of Methyl Bromide to Terrestrial Plants (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Plant Species	Dose/Exposure	Response	Reference
sweetgum seedlings	Field study. Soil injection of a methyl bromide (98%)-chloropicrin (2%) formulation applied at rate of 390 kg/ha (not specified if this is a.i. or formulation), plots were tarped. Seedlings planted 6 days after application.	Examined effects of soil fumigation on seedling height, root collar diameter, root morphology, vesicular-arbuscular mycorrhizal (VAM) infections, soil-borne spore number, and soil fertility. In methyl bromide treated plots, decrease in seedling height, root collar diameter, and VAM infections. After 1 growing season, no difference detected in seedling height, but root collar diameter remained decreased. No significant effects on soil-borne spore number or soil fertility.	Snyder and Davey 1986
rice (2 varieties: Calrose and Caloro)	Germination study, with exposures conducted in an airtight chamber. Methyl bromide concentrations of 1.5, 2.0, 2.5, and 3.0 lb/1000 ft ³ . Exposure periods of 2, 8, and 24 hours at temperatures of 50, 70, and 90°C. Moisture content of seeds of 8, 10, 12, and 14%. Some repeated exposures	Effect of methyl bromide exposure measured as dead seeds. Reduction in germination observed with increasing dose, exposure period, temperature, number of exposures and, in general, seed moisture content. No notable differences observed between varieties.	Strong and Lindgren 1959

Appendix A3: Effects Data: Toxicity of Methyl Bromide to Terrestrial Plants (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Plant Species	Dose/Exposure	Response	Reference
Seed viability study with barley, corn, grain sorghum, oats, wheat seeds	Germination study. Seed fumigation with 2, 4, 6, 8 lbs/1000 ft ³ methyl bromide for exposure periods ranging from 4-24 hours. Tested under a variety of conditions (moisture content of seeds, temperature, storage condition and length of exposure after fumigation, size of fumigation space relative to commodity volume.	Overall relative order of tolerance: oats >barley >grain sorghum >corn >wheat Little or no injury was observed at application rates of 2 lbs/1000 ft ³ for less than 24 hours, under most experimental conditions Extensive germination damage can be observed under various experimental conditions. General observations: Germination decreased with increasing moisture content of seeds, increasing dose of methyl bromide and increasing exposure period.	Whitney et al. 1958

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
MICROORGANISMS			
Fusarium oxysporum, Pythium, Rhizoctonia (fungal pathogens).	Methyl bromide (2 lb/100 ft ²) applied to nine chrysanthemum varieties	No Fusarium detected in soil. Good control of Pythium, Rhizoctonia, but neither was completely controlled No phytotoxicity observed to any chrysanthemum variety	MRID 00010245 (Crane and Mellinger 1974)
<i>Armillaria mellea</i> (causes oak root fungus)	Field study in vineyard. Methyl bromide applied at 300 and 400 lb/acre under tarp	Nearly total control of <i>Armillaria mellea</i> at 300 lb/acre rate. Total control of <i>Armillaria mellea</i> at 400 lb/acre rate.	MRID 00013029 (Kissler et al. 1973)
fanleaf virus	Field study. Methyl bromide applied at 400-800 lb/acre under tarp	good control over fanleaf virus	MRID 00013030 (Raski and Schmitt 1972)
<i>Armillaria mellea</i> (fungus)	Infected roots treated with methyl bromide in air at exposures ranging from 500 to 2200 ppm for 1 to 16 days	increase in control of fungal populations with increasing does and time of exposure	MRID 00013163 (Munncke et al. 1970)
<i>Armillaria mellea</i> (fungus) and Trichoderma sp. (fungus)	Laboratory study of fungal infections of roots. Methyl bromide exposure ranged from 5-67 mL a.i./2L air for 4 days	<i>Armillaria mellea</i> was more sensitive than Trichoderma sp. Both populations were significantly decreased by methyl bromide	MRID 00013174 (Ohr et al. 1973)

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
soil mycoflora	Greenhouse study of soil growing tomatoes. 75 g/m ² methyl bromide (98% with 2% chloropicrin). Soil samples tested for mycoflora after 4, 12, 30 and 60 days after treatment. Soil depths tested: 0-10, 11-20, 21-30, and 31-40 cm.	105 species of mycoflora present before treatment. At all depths, nearly complete eradication of soil mycoflora at 4 and 12 days. Populations started to recover at 30 days, but did not reach control levels by 60 days after treatment. Re-colonization rate was slowest in the 21-30 cm sample. Some species appear resistant to methyl bromide: <i>Aspergillus alutaceus</i> , <i>Paecilomyces lilacinus</i> , <i>Penicillium crhysogenum</i> , <i>P. funiculosum</i> , <i>P. herquei</i> , <i>Trichoderma barzianum</i> , and <i>T. veridae</i> .	Bourbos and Skoudridakis 1991
soil pathogens – fungi (<i>Fusarium</i> , <i>Pythium</i> , and <i>Rhizoctonia</i>)	Field study. 100% methyl bromide (application rate not specified) applied to plots of white pine seedlings	populations of pathogens remained decreased for 9 months after application	Enebak et al. 1988
soil pathogens – fungi (<i>Fusarium</i> , <i>Pythium</i> , and <i>Rhizoctonia</i>)	Field study. 100% methyl bromide (392 kg/ha) applied by soil injection to plots of white pine seedlings and tarped for 5 days	9 months after treatment, populations of soil fungi remained low in methyl bromide treated plots. Compared to control, density of white pine seedlings/plot was increased in methyl bromide treated plots and seedling taproots were longer.	Enebak et al. 1990
<i>Armillariella mellea</i> (soil fungus)	Field study – fumigation of ponderosa pine stumps with 100% methyl bromide by injection into stumps, at application rates ranging from 0.056 to 10 mL/cm ³ wood.	Methyl bromide application eradicated fungus from stumps	Filip and Roth 1977

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
<i>Phytophthora parasitica</i> (fungus)	Field study. 67% (with 33% chloropicrin and 98% (with 2% chloropicrin) Methyl bromide released at soil surface under tarps. Application rates range from 0.25 to 1.0 lb/ft ² .	<i>P. parasitica</i> populations tested at various depths up to 4 feet. Dose require to kill organisms increased with increasing soil depth.. At rate of 1.0 lb/ft ² , all organisms were killed at depths up to 4 ft.	Grimm and Alexander 1971 same data reported in Grimm and Alexander 1971 MRID 00013161
<i>Xiphinema diversicaudatum</i> and arabis mosaic virus (AMV) (spread by <i>X. diversicaudatum</i>)	Field study. Methyl bromide applied at rate of 2 lb/ft ² to plots of strawberries	Treatment effective in killing <i>X. diversicaudatum</i> in soil and decreasing the incidence if AMV infection of strawberry plants	Harrison et al. 1963
microorganisms in poultry houses	0, 10, 20, and 40 mg/L (gas) 25°C for 20 hrs	Dose-related decrease in viability of all organisms tested. Most sensitive species: <i>E.coli</i> Most tolerant species: <i>Salmonella typhimurium</i>	Harry et al. 1972
<i>Scelrotinia scelerotiorum</i> (fungus)	Field study in tobacco seed beds. Methyl bromide applied at 50g/m ² and covered with tarps	complete suppression of fungal growth	Harthill and Campbell 1973
<i>Byssoschlamys fulva</i> (mold)	60 and 90 mg methyl bromide/kg tapioca starch in sealed flasks	Methyl bromide was effective in controlling mold growth for 30 days	Ito et al. 1972
soil fungal pathogens (<i>Phytophthora nicotianea</i> , <i>Fusarium solani</i> , <i>Fusarium oxysporum</i>)	Pre-plant soil fumigation with 49 and 98 g/m ² methyl bromide in replant area of citrus trees	One week after fumigation, no fungi detected.	Le Roux et al. 1998
<i>Corynbacterium sepedonicum</i> (potato ring rot bacteria)	Laboratory study to mimic space fumigation of bags of potatoes. Methyl bromide exposure for 18 to 48 hours at concentrations of 5, 10 and 15% methyl bromide.	Bacterial growth was decreased, but complete control was not achieved.	Richardson and Monro 1965
<i>Xanthomonas Begoniae</i> (pathogenic soil bacteria)	Greenhouse study. Methyl bromide (2 lb/100 ft ³) applied to clay pots growing begonia	Soil fumigation with methyl bromide completely eliminated bacteria from infected begonia tissue buried in soil.	Strider 1975

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
Several species of soil fungi	Field study. Methyl bromide injected into soil at 200 and 300 lb/acre and covered with tarps	Several species of soil fungi were "controlled".	Thomason 1959
<i>Fusarium</i>	Field study in petunia plots. Methyl bromide with chloropicrin (2%) (application rate not specified)	Significant improvement in plant vigor. No measurement of effect on soil population of <i>Fusarium</i> .	Weihing et al. 1971
fungi infecting weevil-damaged pecans	methyl bromide 0.8, 1.6, 3.3 kg/100 m ³ ,	applications of 1.6 and 3.3 kg/100 m ³ effective in controlling fungal infection in weevil-damaged pecans.	Wells and Payne 1975
		Most sensitive fungi: <i>Fusarium</i> and <i>Pestalotia/Monochaeta</i> Most tolerant fungus: <i>Penicillium</i>	
<i>Fusarium oxysporum</i>	Greenhouse study with tomato plots. Methyl bromide applied at 100 g/m ² and tarped	Nearly complete eradication of soil <i>Fusarium</i>	Weststeijn 1973
club root fungus (<i>Plasmodiophora brassicae</i>)	Field study. Methyl bromide applied to cabbage plots at 1, 2, and 3 lb/100 ft ²	All applications gave excellent control over the development of clubroot.	Winstead and Garriss 1960
<i>Fusarium oxysporum</i> (parasite for hothouse tomatoes)	75 g/m ² 25°C for 24 hrs	Disinfected soil content to a depth of 15 cm	Vanachter 1974
INSECTS			
Several insects	Review No data reported in this paper	Use of methyl bromide as a space fumigant is effective in controlling confused flour beetle, granary weevil, German cockroaches, cheese skippers, cheese mites, corn borer, rice weevils, red flour beetle, lesser grain borer, Indian-meal moth, Kharpa beetle, tobacco moth, and several wood boring insects.	MRID 00114033 (Dow Chemical Company 1974)

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
comstock mealy bug	Field study. Methyl bromide applied at 2.5 lb/1000 ft ³ for 2 and 2.5 hours	Methyl bromide effective at killing eggs	MRID 00116551 (Vettek 1971)
<i>Callosobruchus chinensis</i> (cow pea or black weevil)	24-hour exposure to methyl bromide in sealed flasks. Dose range and formulation not specified)	LC ₅₀ values for the following growth stages – eggs: 0.851 mg/L larva: 2.208 mg/L pupa: 0.891 mg/L adults: 1.67 mg/L	Adu and Muthi 1985
12 strains of 7 beetle species	Laboratory space fumigation study at 15 and 25°C. Methyl bromide concentration range of 0.6-3.0 mg/L at 15°C, and 1.3-4.0 at 25°C for variable exposure periods	In all strains, methyl bromide more effective at 25°C than 15°C. High variability between species for susceptibility to methyl bromide.	Bell 1988
cadelle beetle	Laboratory fumigation study. Exposure to 10, 16, and 23 mg/L methyl bromide for 5 hours	Insects with a high normal respiratory rate were more susceptible to methyl bromide than insects with a low respiratory rate. Pre-exposure of beetles to low doses of methyl bromide did not result in an increase in LD ₅₀ values.	Bond 1956
<i>Acarus siro</i> (cheese-infecting mite)	Laboratory fumigation. Exposure to various concentrations of methyl bromide for 4, 8, 16, and 24 hours.	LC ₅₀ values for various exposure times: 4-hour LC ₅₀ = 9.13 mg/L 8-hour LC ₅₀ = 4.61 mg/L 16-hour LC ₅₀ = 2.47 mg/L 24-hour LC ₅₀ = 1.69 mg/L	Burkholder 1966
codling moth eggs	Mechanisms of action study. Eggs exposed to 48 g/m ² methyl bromide (a.i.) for 2 hours.	1 hour after exposure, cell division stopped. Cells of surviving eggs showed general characteristics of neoplastic cells. Methyl bromide appears to act as a general cell toxin.	Cheetham 1990

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
codling moth larvae	Mechanism study. Laboratory fumigation of larvae to 3.6-9.6 g/m ³ methyl bromide for 2 hours.	Examination of changed in ventral nerve cord and ganglia. Changes observed in perineural glial cells (membrane disruption, dilation of endoplasmic reticulum, vacuolization of cytoplasm). Mechanism of action appear to be through disruption of normal neuronal function	Cheetham 1992
<i>Cydia pomonella</i> (codling moth)	Space fumigation, recirculating method, 2-hour fumigation	Effects examined on freshly laid eggs and diapausing 5 th instars. Mortality observed for both eggs and 5 th instars, with eggs being more tolerant than 5 th instars	Dentener et al. 1998
<i>Plodia interpunctella</i> (Indian meal moth)	Fumigation of flour mill. Application rate not specified	Decrease on moth population at various locations around the mill	Doud and Philips 2000
<i>Corcyra cephalonica</i> (rice moth)	Lab study. Space fumigation in sealed glass bottles. Methyl bromide concentrations ranging from 0.63 to 4.051 mg/L for 5 hours	Conclusions: 1. Adult diet did not affect susceptibility of eggs 2. 3-day old eggs more susceptible than 1-day old eggs 3. Diet did not affect susceptibility of 1 st larval instars 4. Addition of yeast or yeasts and casein to diet decreased susceptibility of 3 rd and last larval instars 5. Wheat bran diet increased susceptibility of 3 rd and last larval instars 6. Larger larvae are more resistant 7. Diet may slightly affect susceptibility of 3-day old pupae LC50 values given for 6 different diets and 6 different growth stages	El-Buzz et al. 1974

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
7 species of beetles, all growth stages	Laboratory experiment in fumigation chamber. Methyl bromide concentration in chamber approximately 4.0 mg/L. Exposure time variable (4 - 48 hours), depending on species	In all species, egg and pupal stages were more tolerant than larval and adult stages. Large variability in susceptibility between species.	Hole 1981
overwintering corn borer (<i>Ostrinia nubilalis</i> and <i>Chilo aggramemnon</i>)	Field study. Methyl bromide (ampules - formulation not specified) applied to piles of corn stalks at 16, 20, 24, and 28 g/m ³ for 8, 16, and 24 hours. Stacks covered with plastic tarps	Similar results for both species: For 8 and 16 hours exposures, dose-dependent mortality observed. For 24 hour exposure, all doses produced 100% mortality	Isa et al. 1970
<i>Oryzaephilus mercator</i> (merchant grain beetle)	Laboratory fumigation study. 0.5 to 2 hour exposure to 0.2 g/L	Methyl bromide effective in killing larvae and adults. 100% adults and larvae killed after 1 and 2 hour exposure to methyl bromide.	Joshi 1974
<i>Tribolium confusum</i> (flour beetle)	Laboratory fumigation study conducted at 3 temperatures (40, 60, and 80°C) and 3 exposure periods (2, 5, and 16 hours).	Methyl bromide effectiveness increased with increasing exposure time and increasing temperature.	Kenaga 1960
<i>Acarus siro</i> (mite)	Space fumigation study on eggs. Methyl bromide exposure of 40g/m ³ for 24 hours. Mechanism study.	Exposure of 0, 1, 2, 3, 4, and 5 day old eggs. Integument of eggs became sticky, non-elastic and soft. Changes in developing nervous system were observed. Deformity of embryos observed,	Klag and Komorowska 1975
Several peanut pests: almond moth, Indian meal moth, red flour beetle, merchant grain beetle	Methyl bromide applied to bags of peanuts at a dose of 32 mg/L (over 24 hours).	Insect infestations were controlled	Leesch et al. 1974

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
<i>Cydia pomonella</i> (codling moth)	space fumigation study on plums at exposure of 22.5 and 48 g/m ³	eggs on plums were controlled by doses of 22.5 and 48 g/m ³	Leesch et al. 1999
<i>Incisitermes minor</i> (Western drywood termite)	Space fumigation study with CO ₂ -synergized methyl bromide, 1.4 kg/177.8m ³	termite mortality was 100% 3 days after treatment	Lewis and Havery 1996
pea leafminer	Laboratory study. Fumigation of insects with methyl bromide in sealed chambers (approximately 13.5 mg/L)	LD₅₀ values: eggs: 23.3 mg/L•hr larvae (< 7 days): 15.5 mg/L•hr larvae (> 7 days): 14.4 mg/L•hr pupae: 22.9: 15.5 mg/L•hr	Macdonald and Mitchell 1996
<i>Graphognathus leucoloma</i> (white-fringed beetle)	Laboratory fumigation study. Exposure of 1 st instar larvae to methyl bromide (concentrations not specified) for 24 hours	Efficacy of methyl bromide on 1 st instar white-fringed beetle (soil dwelling). Dose-related increase in mortality of larvae.	Mathiessen et al. 1996
<i>Ephestia kuehniella</i> (Mediterranean flour moth), <i>Sitotroga cerealella</i> , (Angoumois grain moth), <i>Tribolium castaneum</i> (Red flour beetle), and <i>Sitophilus oryzae</i> (Rice weevil)	Laboratory fumigation study. Exposure to methyl bromide (1.2-2.4 mg/L for moths and 3.5-8.0 for beetles) for 5, 6, or 7 hour exposure periods.	Examined susceptibility of 1, 2, and 3 day old eggs. Older eggs more susceptible. Effectiveness increased with increasing exposure period.	Mostafa and Kamel 1972
brown dog tick	Laboratory study methyl bromide doses of 32-144 mg/L	almost 100% mortality at all doses. Efficacy reduced at temperatures below 10°C	Roth 1973
<i>Anthonomus grandis</i> (boll weevil, Ebony Pearl strain)	Laboratory fumigation study. Exposure to methyl bromide concentrations ranging from 16-96 mg/L for 1-16 hours at several temperatures (0.6-35°C)	100% mortality or nearly 100% under all experimental conditions.	Roth and Kennedy 1972

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
<i>Plodia interpunctella</i> (Indian meal moth)	Laboratory study. Space fumigation in vials to methyl bromide doses ranging from 6.0-18.04 mg/L for 1 hour	diapausing (hibernating) insects less susceptible than non-diapausing (normal) insects. Methyl bromide appears to accelerate respiration of the diapausing insect (based on increased CO ₂ output)	Sardesai 1972
10 species of Nearctic termite	Laboratory fumigation study. Exposure to methyl bromide (concentration range not specified) for 20 hours at 27°C	All species of termites were susceptible to methyl bromide. Wide range of susceptibility was observed between species.	Scheffrahn and Su 1992
<i>Trogoderma variable</i> (warehouse beetle)	Laboratory study. Exposure to methyl bromide concentrations ranging from 8-40 mg/L at 3 temperatures (15.6, 21.1, and 26.7°C) for 2-24 hours	Eggs and post-embryonic growth stages. Effectiveness increased as exposure time and temperature increased. Very little difference between growth stages regarding sensitivity.	Vincent and Lindgren 1975
<i>Maconellicoccus hirsutus</i> (pink hibiscus mealybug)	Laboratory study. 2-hour fumigations to methyl bromide concentrations ranging from 8-64 mg/L at 25°C and a relative humidity of 95%	Dose-response study; all stages tested (eggs, crawlers, early nymphs, late nymphs, and adults). Based on LD ₅₀ values, eggs were most susceptible. No difference in response of all active life stages. LD ₅₀ values – eggs: 7.1 mg/L crawlers: 25.1 mg/L early nymphs: 26.5 mg/L late nymphs: 25.0 mg/L adults: 25.7 mg/L Methyl bromide was effective in controlling pink hibiscus mealybug. All stages completely controlled following exposure to 48 mg/L for 2 hours.	Zettler et al. 2002

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
NEMATODES			
nematodes: <i>Trichodorus</i> , <i>Belonolaimu</i> , rootknot, and <i>Hemicycliophora</i>	Field study. Methyl bromide applied by soil injection (rate not specified) to plots of tomatoes	Decrease in soil populations of all nematodes. Decrease in wilt of tomato plants	MRID 00010152 (Walters 1974)
<i>Xiphinema index</i> (dagger nematode)	Field study. Methyl bromide applied at 400-800 lb/acre under tarp	Nearly total eradication of nematodes	MRID 00013030 (Raski and Schmitt 1972) Data also reported in Soil Chemical Corp. 1972 MRID 00118839
nematodes (cannot read fiche for specific nematode type)	Field study. Vineyards treated with methyl bromide (cannot read application rate on fiche)	good control over nematodes in soil	MRID 00013031 (Schmitt 1970)
Nematodes	Greenhouse study. 24 hour exposure to the to methyl bromide in soil at concentrations ranging from 200to 800 ppm (same concentrations were not used for each type of nematode)	<i>Xiphinema index</i> 24-hr LC ₅₀ = 200-250 ppm <i>Meloidogyne incognita</i> 100% mortality at 600-650 ppm <i>Heterodera schachtii</i> 100% mortality at 750-800 ppm	MRID 00013032 (Lear 1972)
Four plant-parasitic nematodes: <i>Paratylenhucus</i> spp., <i>Heterodera schachtii</i> , <i>Meloidogyne incognita</i> , <i>Xiphinema index</i>	Fumigation of nematode-infested soil in cans. Exposure to methyl bromide for 1-21 days at concentrations in soil ranging from 20-2500 ppm.	Toxicity varied with species as follows, with increasing sensitivity: <i>Paratylenhucus</i> spp., <i>Heterodera schachtii</i> , <i>Meloidogyne incognita</i> , <i>Xiphinema index</i> Toxicity increased with increasing temperature, exposure time and dose.	Abdalla and Lear 1975

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
<i>Hoplolarimus columbus</i> and <i>Pratylenchus brachyurus</i> (nematodes infecting cotton)	Greenhouse study. Soil treated with methyl bromide (454g/16 pots; pot size: 40 cm) then planted with cotton	Marked reduction in soil content of nematodes	Bird et al. 1974
root-knot nematode	Field study (white clover plots). Methyl bromide applied at 1 lbs/100 ft ² . 4 applications	Methyl bromide provided good control over nematode population for up to 3 years after initial treatment	Chen et al. 1962
nematodes	Field study. Methyl bromide with chloropicrin (2%) 871 lb/acre applied to celery seed beds	Significant reduction in nematode population up to 150 days after treatment	Darby et al. 1962
<i>Meloidogyne javanica</i> (root knot nematodes)	Field study. methyl bromide applied at 70 g/m ² one month before planting tomato and melon plants	Dramatic reduction in soil nematode populations and increased plant yield. Re-colonization observed during the second year after treatment, with decreased plant yields.	Eddaoudi and Bourijate 1998
<i>Steinernema carpocapsae</i> (entomopathogenic nematode)	Laboratory study. 0.45 kg methyl bromide gas, sealed container for 2 days	Nematode infectivity of wax moth larvae decreased for up to 25 days	Gibb and Buhler 1998
moss-living anhyrobiotic organisms (nematodes, tardigrades, and rotifers)	Laboratory study. Methyl bromide gas (50 g/m ³ for 70 hours) in closed containers containing moss collected from the Baltic Sea region	Survival of nematodes decreased. Survival of tardigrades not affected by treatment	Jonsson and Guidetti 2001
<i>Pratylenchus brachyurus</i>	Laboratory study – space fumigation of peanut shells and whole pods of peanuts in 1-liter flasks for 24 hour at 25°C. Methyl bromide (formulation not specified) concentrations ranged from 17.3 to 50.9 mg/L	At 17.3 mg/L, nearly complete eradication of nematodes. At doses \geq 24.5mg/L, complete eradication of nematodes	Minton and Gillenwater 1973

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
3 species of parasites (<i>Tylenchorhynchus</i> , sp., <i>Trichodorus</i> sp., and <i>Pratylenchus zeae</i>)	Field study. Methyl bromide (98% with 2% chloropicrin) applied to soil at application rate of 2 lb/100 ft ² and tarped prior to planting corn	Complete eradication of nematodes 2 weeks after treatment. Populations started to recover after 3 months, but did not reach untreated levels. Compared to controls, higher corn yield in methyl bromide treated plots.	Oakes et al. 1956
<i>Tylenchulus</i> <i>semipenetrans</i> (citrus nematode)	Field study. Pre-plant soil fumigation with 49 and 98 g/m ² methyl bromide in replant area of citrus trees	No nematodes detected 2 years after fumigation. Populations began to recover after 3 years, but did not reach pre-treatment levels after 7 years	Roux et al. 1998
root-knot nematodes (<i>Meloidogyne</i>)	Field study. Chisel application of methyl bromide: 100, 150, and 200 lbs/acre	Dose-dependent decrease in number of nematodes in soil	Sher et al. 1958
nematodes (species not specified)	Field study. Methyl bromide containing chloropicrin (2%) applied to 3 pepper cultivars (application rate not specified)	High control over nematode infestations	Thies and Fery 1997
root-knot nematodes	Field study. Methyl bromide injected into soil at 200 and 300 lb/acre and covered with tarps	nematode populations were "controlled"	Thomason 1959
<i>Heterodera</i> <i>rostoshiensis</i> (potato cyst-nematode)	Field study. Methyl bromide (98%, with 2% chloropicrin) applied to soil (sandy clay) and covered with polyethylene tarp: 111 g/m ²	Decrease in number of larvae invading roots. Increase in number of cysts and eggs in soil. Increase in potato yield	Whitehead et al. 1972

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
<i>Meloidogyne incognita</i> , <i>Xiphinema index</i> , <i>Dorylaimus</i> sp.	Laboratory study. Nematodes in soil growing tomato plants were exposed to "flowing" 600 ppm methyl bromide for up to 132 hours	<i>Meloidogyne incognita</i> became progressively immobile over 38 hours. Infectivity of tomato plants decreased sharply after 30 hours. Results indicate a gradual "narcotization" of nematode. No evidence of "narcotization" in <i>Xiphinema</i> <i>index</i> . Narcotization of <i>Dorylaimus</i> sp. was intermediate.	Van Gundy et al. 1972
nematodes (type not specified)	Laboratory/Field study. Core soil samples fumigated in the laboratory with methyl bromide (48 g/m ³). Samples then returned to field and monitored at 1, 5, 12, 26, 54, 110, and 166 days	Following treatment, no nematodes in soil, until day 26 sampling. At 166 days after treatment, population recovering, but still significantly below untreated samples.	Yeates et al. 1991
OTHER ORGANISMS			
<i>Cochlicella barbara</i> and <i>Theba pisana</i> (snails)	Laboratory fumigation study. Snails exposed to 2 or 3 pounds methyl bromide/1000 ft ³ for 2 hours or 2, 3, 4, 6, and 8 pounds methyl bromide/1000 ft ³ for 24 hours	Most snails survived the 2- hour exposure to methyl bromide. Increasing exposure time and dose resulted in an increase in mortality. <i>Cochlicella barbara</i> more resistant to methyl bromide than <i>Theba pisana</i> .	Richardson and Roth 1965
WEED CONTROL			
weeds (purslane and grasses)	Greenhouse study. Methyl bromide (2 lb/100 ft ²) applied to nine chrysanthemum varieties	Weeds were controlled, but not completely. No phytotoxicity observed to any chrysanthemum variety	MRID 00010245 (Crane and Mellinger 1974)

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
weeds	Field study in strawberry plots. Methyl bromide: chloropicrin (2:1) and methyl bromide alone applied at a rate of 250-300 lbs/acre and tarped	Both treatment showed good control of weeds. Methyl bromide alone was more effective in controlling weeds, but strawberry plants was inferior to that of non-treated plots	MRID 00012926 (Voth et al. 1973)
weeds	Field study. Methyl bromide applied to soil growing loblolly pine at rates of 1 lb/150 ft ² (liquid formulation) released under tarp, 300 lbs/acre (gas formulation released under tarp, and 175 lb/acre injected and covered with tarp	Excellent weed control with all applications. No adverse effect to pine seedlings.	MRID 00013199 (Hodges 1960)
<i>Helicella</i> snails (2 species)	Laboratory test of 2 species of snails infesting rosemary seeds. Methyl bromide applications of 16 - 128 mg/L for 3 hours	High level of mortality at all treatment levels	Roth and Kennedy 1973
weeds (not specified)	Field study. Methyl bromide with chloropicrin (2%) 871 lb/acre applied to celery seed beds	total weed control observed	Darby et al. 1962
wirestem and other weeds	Field study. Methyl bromide applied to cabbage plots at 1, 2, and 3 lb/100 ft ²	All applications controlled growth of wirestem (a weed) and other weeds.	Winstead and Garriss 1960

Appendix A4: Effects Data: Efficacy Studies on Methyl Bromide (unless otherwise specified, all concentrations are expressed in terms of a.i.)

Organism	Dose/Exposure	Response	Reference
8 species of weeds	<p>Germination studies (fumigation of seeds): soil application of methyl bromide applied to planted seeds; concentration of methyl bromide in soil – 0, 10, 20, 40, 60, 80, 100, 150, 200, and 400 μM.</p> <p>Vigor studies (direct application to weed plants): methyl bromide applied at rates of 0, 56, 112, 224, 448, and 896 kg a.i./ha</p>	<p><u>Germination studies:</u> Most sensitive species: <i>Amaranthus retroflexus</i> (EC_{50} = 24.8 μM)</p> <p>Most tolerant species: <i>Portulaca oleracea</i> (EC_{50} = 160.8 μM)</p> <p><u>Vigor studies:</u> Most sensitive species: <i>Amaranthus retroflexus</i> (EC_{50} = 71.8 kg a.i./ha)</p> <p>Most tolerant species: <i>Cyperus rotundus</i> (EC_{50} = 143.1 kg a.i./ha)</p>	Zhang et al. 1997
MAMMALS			
Black-Tailed Prairie Dog	<p>Field study.</p> <p>Methyl bromide gas (100% a.i.) and methyl bromide gas (98% a.i.) with chloropicrin (2%).</p> <p>For both formulations, approximately 10 mL applied to each burrow</p>	Both formulations reduced burrow activity by 96% (no details regarding how burrow activity was assessed)	MRID 43467501 (Hygnstrom 1994)

Appendix A5: Effects Data: Toxicity of Bromide Ion

Animal	Dose/Exposure	Response	Reference
Fish			
medaka (<i>Oryzias latipes</i>) and guppy (<i>Poecilia reticulata</i>)	<u>Acute Exposure</u> of guppies and medaka to sodium bromide for 4 days.	Acute exposure results: <u>guppy</u> 96-hour LC₅₀ = 16 g Br ⁻ /L 96-hr EC₅₀ (abnormal behavior) = 0.044 g Br ⁻ /L 96-hr NOLC = 7.8 g Br ⁻ /L 96-hr NOAEC = 0.025 g Br ⁻ /L	Canton et al. 1983
	<u>Long-term Exposure</u> to sodium bromide in guppies for 28 days and 124 days and medaka (eggs and fry study) for 34 days. Concentration ranges not specified	<u>medaka</u> 96-hour LC₅₀ = 24 g Br ⁻ /L 96-hr EC₅₀ (abnormal behavior) = 0.044 g Br ⁻ /L 96-hr NOLC = 7.8 g Br ⁻ /L 96-hr NOAEC = 0.25 g Br ⁻ /L Long-term exposure results: <u>guppy</u> 28-day LC₅₀ = 12 g Br ⁻ /L 28-day NOAEC (mortality and behavior) = 2.5 g Br ⁻ /L 124-day LC₅₀ > 7.8 g Br ⁻ /L 124-day NOEC (reproductive effects) = 0.0078 g Br ⁻ /L <u>medaka</u> 34-day LC₅₀ > 1.5 g Br ⁻ /L 34-day NOLC (mortality) = 0.78g Br ⁻ /L 34-day NOAEC (egg hatching) ≥ 7.8g Br ⁻ /L 34-day NOEC (growth) = 0.78g Br ⁻ /L	

Appendix A5: Effects Data: Toxicity of Bromide Ion

Animal	Dose/Exposure	Response	Reference
guppy (<i>Poecilia reticulata</i>) and medaka (<i>Oryzias latipes</i>)	guppies exposed to sodium bromide (10 - 32000 mg/L) for 1 and 3 months.	Sodium bromide was goiterogenic in both species.	Webster et al. 1988
	medaka (embryos) exposed to sodium bromide (180 - 5600 mg/L) for 3 weeks and 3 months.	<u>guppies</u> : In 32,000 mg/L group, all fish died within 2 days of exposure. At concentrations > 32 mg/L, clinical signs of toxicity observed (reduced mobility, immobility, incoordinate movements)	Some results also reported in Webster and Vos 1994
	sodium bromide was technical grade.	<p>1-month NOAEC (lethality) = 10,000mg/L</p> <p>3-month NOAEC (lethality) = 1000mg/L</p> <p>1-month NOAEC (toxicity) = 32 mg/L</p> <p>3-month NOAEC (toxicity) = 32 mg/L</p> <p><u>medaka</u>: At concentrations > 320 mg/L, clinical signs of toxicity observed (reduced mobility, immobility, incoordinate movements).</p> <p>3-week NOAEC (lethality) = 5,600 mg/L</p> <p>3-month NOAEC (lethality) = 3200mg/L</p> <p>3-week NOAEC (toxicity) = 320 mg/L</p> <p>3-month NOAEC (toxicity) = 320 mg/L</p>	

Appendix A5: Effects Data: Toxicity of Bromide Ion

Animal	Dose/Exposure	Response	Reference
Aquatic Invertebrates			
<i>Daphnia magna</i>	<p><u>Acute Exposure</u> to sodium bromide for 2 days.</p> <p><u>Long-term Exposure</u> to sodium bromide for 19 and 23 days</p> <p>Concentration ranges not specified</p>	<p>Acute exposure results:</p> <p>48-hour LC_{50} = 11 g Br⁻/L</p> <p>48-hr EC_{50} (toxicity) = 5.8 g Br⁻/L</p> <p>48-hr NOAEC (mortality) = 7.8 g Br⁻/L</p> <p>48-hr NOAEC = 0.025 g Br⁻/L</p> <p>Long-term exposure results:</p> <p>19-day LC_{50} = 6.1 g Br⁻/L</p> <p>Dose-dependent decrease in total number of eggs produced per female and in egg viability.</p> <p>For 23-day exposures, reproductive capacity was reduced, with an NOAEC = 0.0078 g Br⁻/L</p>	Canton et al. 1983
<i>Daphnia magna</i>	Exposure to sodium bromide at concentrations of 0, 4.5, 8.6, 16.3, 27.9, 45.0, and 98.0 mg/L for up to 20 days	<p>ALL RESULTS ARE FOR SODIUM BROMIDE</p> <p>EC_{50} (impairment of reproduction) = 27 mg/L</p>	van Leeuwen et al. 1986
Algae			
Green algae (<i>Scenedesmus quadricauda</i>)	<p><u>Acute Exposure</u> to sodium bromide for up to 96 hours.</p> <p>Concentration range not specified</p>	<p>48-hour LC_{50} (growth) = 7.8 g Br⁻/L</p> <p>48-hr EC_{50} (growth) = 2.5 g Br⁻/L</p> <p>96-hour LC_{50} (growth) = 10 g Br⁻/L</p> <p>96-hr EC_{50} (growth) = 2.5 g Br⁻/L</p>	Canton et al. 1983

Appendix B: Environmental Fate Data

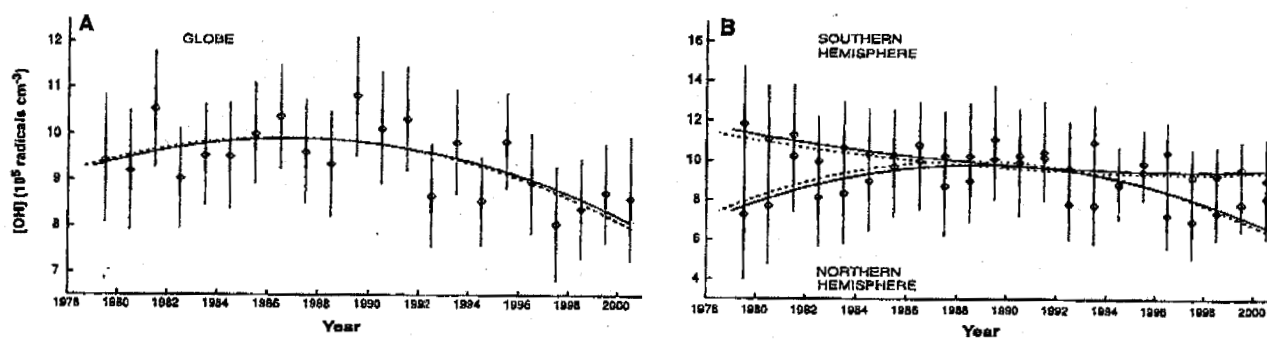


Figure B1. Hydroxyl radical concentration as a function of time. Reproduced from Prinn et al. 2001.

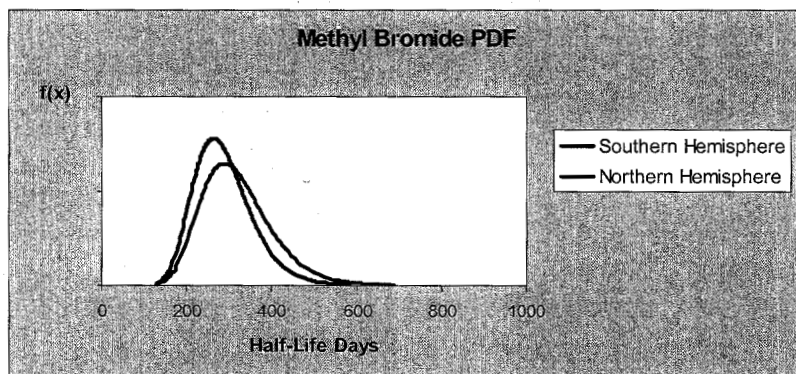


Figure B2. Probability density function for the atmospheric half-life of methyl bromide in the Northern and Southern Hemisphere

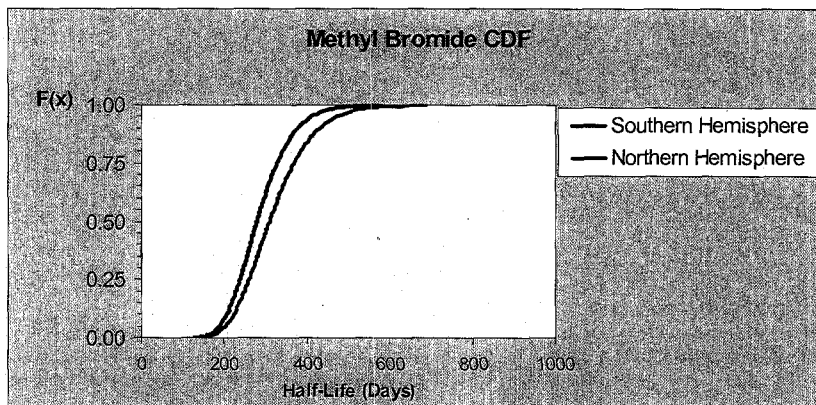


Figure B3. Cumulative distribution function for the atmospheric half-life of methyl bromide in the Northern and Southern Hemisphere.

SOURCES AND SINKS OF METHYL BROMIDE

Although anthropogenic sources have contributed to the release of methyl bromide, the greatest environmental source of methyl bromide arises naturally from biogenic origins. The ocean is both a major source and sink for methyl bromide. Current estimates suggest that about 56 Gg (5.6×10^7 kg) of methyl bromide are emitted from the ocean and uptake is about 77 Gg (7.7×10^7 kg) annually, resulting in a net sink of about 21 Gg (2.1×10^7 kg) (Baker et al. 1999). Others have suggested that these numbers are slightly higher, but still conclude that the ocean acts as a net sink for methyl bromide (Butler and Rodriguez 1996; WMO 2002). The combustion of vegetation (biomass burning) is another significant natural source of methyl bromide to the atmosphere. Approximately 20 Gg (2.0×10^7 kg) of methyl bromide are released each year from the burning of biomass (Butler and Rodriguez 1996). Coastal salt marshes have also been identified as a natural terrestrial source of methyl bromide, with emissions of about 14 Gg (1.4×10^7 kg) annually, and recently the production of methyl bromide and methyl chloride was demonstrated in laboratory studies using a variety of terrestrial plants and wood rot fungi (Rhew et al. 2001). A summary of all the different sources and sinks of methyl bromide were presented in the World Meteorological Organization in their most recent document on ozone depletion (WMO 2002), and are shown in table B1.

Table B1. Methyl bromide sources and sinks^a

Source or Sink	Best Estimate (Gg/year)	Possible Range (Gg/year)
Sources		
Ocean	63	23-119
Fumigation of soils	26.5	16.0-48.0
Fumigation of durables	6.6	4.8-8.4
Fumigation of perishables	5.7	5.4-6.0
Fumigation of buildings and structures	2.0	2.0
Leaded gasoline	5.0	0.0-10.0
Biomass burning	20.0	10.0-40.0
Wetlands	4.6	2.3-9.2
Saltmarshes	14.0	7.0-29.0
Shrublands	1.0	0.5-2.0
Rapeseed	6.6	4.8-8.4
Rice fields	1.5	0.5-2.5
Fungus	1.7	0.5-5.2
Peatlands	0.9	0.1-3.3
<i>subtotal(sources)</i>	159	77-293
Sinks		
Ocean	-77	-37 to -133
Photochemical	-80	-60 to -100
Soils	-47	-32 to -154
Plants	Not quantified	Not quantified
<i>Subtotal (sinks)</i>	-204	-129 to -387
Total (Sources + Sinks)	-45	-220 to 71

^a WMO 2002

The high degree of uncertainty reflected in table B1 makes quantifying the global budget of methyl bromide in the atmosphere challenging because this amount is a direct function of the magnitude of its emission sources and sinks.

Appendix C:

PRZM / EXAMS Modeling Inputs/Outputs for Ecological and Drinking Water Risk Assessment

This appendix documents the output from PRZM / EXAMS simulations for each of four location/crop scenarios: California / Tomato, Florida / Strawberry, California / Grape, and North Carolina / Tobacco. The settings for each model run are presented first, followed by the raw data sorted by year and sorted in descending order by EEC. Values represent the estimated environmental concentrations (EECs) in units of micrograms per liter ($\mu\text{g/L}$) or parts per billion (ppb). The 1-in-10 year summary statistics for each run are presented at the very end of the sorted results in the row assigned a probability level of 0.10. This summary statistic was generated from a linear interpretation of the raw data plotted using Weibull plotting positions. This approach is further described at the end of the appendix (Section C.6).

In addition, PRZM / EXAMS simulations were run for the Index Reservoir for each scenario. Estimated drinking water concentrations (EDWCs) for the Florida Strawberries are presented here; results for other scenarios yield lower concentrations.

The raw data are also save to the following Microsoft Excel file, included as a deliverable with this report: Mebr_EECs_CAM4_v2.xls.

C.1.1. Input assumptions for California, Tomato scenario.

Output File: MeBR					
Metfile:	met18.met				
PRZM scenario:	CAtomatoC.txt				
EXAMS environment file:	O134POND.EXV				
Chemical Name:	MeBR				
Description	Variable Name	Value	Units	Comments	
Molecular weight	mwt	94.94	g/mol		
Henry's Law Const.	henry	0.007	atm-m ³ /mol		
Vapor Pressure	vapr	1620	torr		
Solubility	sol	15200	mg/L		
Kd	Kd		mg/L		
Koc	Koc	18	mg/L		
Photolysis half-life	kdp	9	days	Half-life	
Aerobic Aquatic Metabolism	kbacw	15	days	Half-life	
Anaerobic Aquatic Metabolism	kbacs		days	Half-life	
Aerobic Soil Metabolism	asm	22	days	Half-life	
Hydrolysis:	pH 7	11	days	Half-life	
Method:	CAM	4	integer	See PRZM manual	
Incorporation Depth:	DEPI	25	cm		
Application Rate:	TAPP	448	kg/ha		
Application Efficiency:	APPEFF	1	fraction		
Spray Drift	DRFT	0	fraction of application rate applied to pond		
Application Date	Date	15-1	dd/mm or dd/mm or dd-mm or dd-mmm		
Record 17:	FILTRA				
	IPSCND	1			
	UPTKF				
Record 18:	PLVKRT				
	PLDKRT				
	FEXTRC	0			
Flag for Index Res. Run	IR	Pond			
Flag for runoff calc.	RUNOFF	none	none, monthly or total(average of entire run)		

Copied from Mebr_EECs_CAM4_v2.xls.

C.1.2. EECs for California, Tomato scenario, sorted by year.

California Tomato / Pond Scenario							
stored as MeBR.out Chemical: MeBR PRZM environment: CAtomatoC.txt EXAMS environment: O134POND.EXV Metfile: met18.met Water segment concentrations (ppb)							
modified Friday, 5 April 2002 at 07:09:58 modified Weddday, 19 January 2000 at 03:32:56 modified Tuesday, 11 August 1992 at 10:54:46							
Year	Peak	96 hr	21 Day	60 Day	90 Day	Yearly	
1961	4.74	3.39	1.30	0.46	0.31	0.08	
1962	5.60	4.21	1.77	0.97	0.65	0.16	
1963	3.57	2.57	1.23	0.45	0.30	0.07	
1964	3.89	2.70	0.93	0.33	0.22	0.05	
1965	0.15	0.10	0.03	0.01	0.01	0.00	
1966	1.30	0.91	0.30	0.11	0.07	0.02	
1967	18.26	12.43	5.03	1.82	1.21	0.30	
1968	3.78	2.55	0.83	0.34	0.23	0.06	
1969	92.84	69.29	29.16	11.23	7.49	1.85	
1970	406.00	274.00	96.82	34.37	22.92	5.65	
1971	0.00	0.00	0.00	0.00	0.00	0.00	
1972	12.84	8.56	2.75	0.97	0.65	0.16	
1973	65.15	46.71	15.97	6.90	4.61	1.14	
1974	0.18	0.12	0.03	0.01	0.01	0.00	
1975	0.36	0.24	0.08	0.03	0.02	0.00	
1976	1.82	1.42	0.69	0.25	0.17	0.04	
1977	0.00	0.00	0.00	0.00	0.00	0.00	
1978	225.00	153.00	49.71	18.73	12.49	3.08	
1979	33.79	27.21	10.29	4.65	3.10	0.76	
1980	169.00	112.00	35.88	14.02	9.35	2.30	
1981	25.88	17.53	7.92	2.86	1.90	0.47	
1982	0.96	0.70	0.26	0.09	0.06	0.02	
1983	32.87	24.32	14.81	6.11	4.07	1.00	
1984	0.86	0.58	0.20	0.07	0.05	0.01	
1985	0.86	0.60	0.21	0.07	0.05	0.01	
1986	24.55	17.25	6.06	2.17	1.44	0.36	
1987	3.11	2.05	0.67	0.24	0.16	0.04	
1988	33.24	22.73	7.62	2.83	1.89	0.46	
1989	2.78	1.75	0.51	0.31	0.20	0.05	
1990	50.08	37.37	14.58	6.12	4.08	1.01	

Copied from Mebr_EECs_CAM4_v2.xls.

C.1.3. EECs for California, Tomato scenario, sorted by EEC (ppb).

Sorted results						
Prob.	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
0.032	406	274	96.82	34.37	22.92	5.652
0.065	225	153	49.71	18.73	12.49	3.08
0.097	169	112	35.88	14.02	9.351	2.3
0.129	92.84	69.29	29.16	11.23	7.486	1.846
0.161	65.15	46.71	15.97	6.901	4.605	1.135
0.194	50.08	37.37	14.81	6.121	4.081	1.006
0.226	33.79	27.21	14.58	6.108	4.073	1.004
0.258	33.24	24.32	10.29	4.648	3.101	0.7647
0.290	32.87	22.73	7.924	2.856	1.904	0.4695
0.323	25.88	17.53	7.617	2.831	1.889	0.4645
0.355	24.55	17.25	6.064	2.166	1.444	0.3561
0.387	18.26	12.43	5.028	1.821	1.214	0.2993
0.419	12.84	8.558	2.751	0.9721	0.6481	0.1594
0.452	5.602	4.206	1.768	0.9674	0.6452	0.1591
0.484	4.736	3.388	1.303	0.4634	0.309	0.07618
0.516	3.891	2.701	1.225	0.4524	0.3016	0.07437
0.548	3.783	2.568	0.9253	0.3392	0.2262	0.05563
0.581	3.574	2.554	0.8341	0.3286	0.2191	0.05388
0.613	3.106	2.053	0.6894	0.3067	0.2045	0.05043
0.645	2.781	1.745	0.6728	0.2485	0.1657	0.04075
0.677	1.823	1.423	0.5148	0.2378	0.1586	0.0391
0.710	1.304	0.9127	0.3046	0.108	0.07198	0.01775
0.742	0.9646	0.7032	0.2551	0.09427	0.06286	0.0155
0.774	0.8595	0.5987	0.2071	0.07357	0.04905	0.01209
0.806	0.8555	0.5782	0.1982	0.07015	0.04677	0.0115
0.839	0.3587	0.2388	0.07659	0.02705	0.01804	0.004448
0.871	0.1824	0.1155	0.03449	0.01273	0.008491	0.002094
0.903	0.1475	0.09937	0.03251	0.01214	0.008091	0.001995
0.935	4.06E-07	3.85E-07	2.99E-07	1.74E-07	1.24E-07	3.16E-08
0.968	7.45E-09	6.81E-09	5.00E-09	2.83E-09	2.02E-09	5.12E-10
0.100	161.4	107.7	35.2	13.7	9.2	2.3
Average of yearly averages:						0.638377234

Copied from Mebr_EECs_CAM4_v2.xls.

C.2.1. Input assumptions for Florida, Strawberry scenario.

Output File: FL_P				
Metfile:	w12842.dvf			
PRZM scenario:	FLstrawberry.txt			
EXAMS environment file:	pond298.exv			
Chemical Name:	MB			
Description	Variable Name	Value	Units	Comments
Molecular weight	mwt		94.94 g/mol	
Henry's Law Const.	henry		0.007 atm-m ³ /mol	
Vapor Pressure	vapr		1620 torr	
Solubility	sol		15200 mg/L	
Kd	Kd		mg/L	
Koc	Koc		10 mg/L	
Photolysis half-life	kdp		9 days	Half-life
Aerobic Aquatic Metabolism	kbacw		15 days	Half-life
Anaerobic Aquatic Metabolism	kbacs		days	Half-life
Aerobic Soil Metabolism	asm		22 days	Half-life
Hydrolysis:	pH 7		11 days	Half-life
Method:	CAM		4 integer	See PRZM manual
Incorporation Depth:	DEPI		25 cm	
Application Rate:	TAPP		448 kg/ha	
Application Efficiency:	APPEFF		1 fraction	
Spray Drift	DRFT		0 fraction of application rate applied to pond	
Application Date	Date	15-8	dd/mm or dd/mmm or dd-mm or dd-mmm	
Record 17:	FILTRA			
	IPSCND		1	
	UPTKF			
Record 18:	PLVKRT			
	PLDKRT			
	FEXTRC		0	
Flag for Index Res. Run	IR	Pond		
Flag for runoff calc.	RUNOFF	none	none, monthly or total(average of entire run)	

Copied from Mebr_EECs_CAM4_v2.xls.

C.2.2. EECs for Florida, Strawberry scenario, sorted by year.

stored as MeBRstrawpond.out Chemical: MeBR PRZM environment: FLstrawberry.txt EXAMS environment: O134POND.EXV Metfile: met154.met Water segment concentrations (ppb)							
				modified Monday, 8 March 2004 at 14:33:00 modified Wedday, 19 January 2000 at 03:32:56 modified Tuesday, 11 August 1992 at 13:54:46			
Year	Peak	96 hr	21 Day	60 Day	90 Day	Yearly	
1961	81.33	49.49	13.91	4.968	3.327	0.8216	
1962	17.26	10.55	5.421	2.105	1.418	0.3507	
1963	20.04	10.89	3.254	1.197	0.8172	0.2033	
1964	38.07	24.64	8.909	3.299	2.218	0.5476	
1965	1.259	0.6995	0.3083	0.2074	0.146	0.0369	
1966	1.522	0.8815	0.2399	0.1381	0.1037	0.02684	
1967	8.165	5.699	2.063	0.7804	0.5369	0.1337	
1968	7.115	3.948	2.003	0.8316	0.5768	0.1433	
1969	58.43	36.07	11.04	4.01	2.689	0.6656	
1970	102	54	15.33	5.493	3.679	0.9091	
1971	691	410	107	37.83	25.25	6.227	
1972	129	76.68	29.37	10.36	6.936	1.707	
1973	23.45	15.61	5.327	2.056	1.388	0.3436	
1974	1.271	0.7705	0.412	0.2051	0.1481	0.03762	
1975	3.926	2.189	0.9584	0.5296	0.3705	0.09264	
1976	108	72.97	19.35	6.957	4.652	1.145	
1977	176	95.41	25.46	9.056	6.052	1.494	
1978	46.49	26.52	7.138	2.623	1.765	0.4367	
1979	33.16	24.67	9.728	3.735	2.508	0.6206	
1980	224	123	34.38	12.18	8.144	2.005	
1981	14.47	8.356	2.698	1.04	0.7066	0.1757	
1982	61.71	36.25	11.42	4.326	2.901	0.717	
1983	6.795	4.24	2.796	1.197	0.8082	0.2007	
1984	33.89	19.98	6.848	2.478	1.666	0.411	
1985	8.807	4.917	1.645	0.6236	0.4356	0.1087	
1986	51.15	29.18	9.752	3.531	2.375	0.587	
1987	9.51	5.214	1.881	0.7301	0.5011	0.1247	
1988	126	71.26	21.67	8.261	5.531	1.363	
1989	8.6	5.707	3.207	1.182	0.8029	0.1996	
1990	0.671	0.4052	0.2048	0.08628	0.05768	0.0145	

Copied from Mebr_EECs_CAM4_v2.xls.

C.2.3. EECs for Florida, Strawberry scenario, sorted by EEC (ppb).

Sorted results							
Prob.	Peak	96 hr	21 Day	60 Day	90 Day	Yearly	
0.032	691	410	107	37.83	25.25	6.227	
0.065	224	123	34.38	12.18	8.144	2.005	
0.097	176	95.41	29.37	10.36	6.936	1.707	
0.129	129	76.68	25.46	9.056	6.052	1.494	
0.161	126	72.97	21.67	8.261	5.531	1.363	
0.194	108	71.26	19.35	6.957	4.652	1.145	
0.226	102	54	15.33	5.493	3.679	0.9091	
0.258	81.33	49.49	13.91	4.968	3.327	0.8216	
0.290	61.71	36.25	11.42	4.326	2.901	0.717	
0.323	58.43	36.07	11.04	4.01	2.689	0.6656	
0.355	51.15	29.18	9.752	3.735	2.508	0.6206	
0.387	46.49	26.52	9.728	3.531	2.375	0.587	
0.419	38.07	24.67	8.909	3.299	2.218	0.5476	
0.452	33.89	24.64	7.138	2.623	1.765	0.4367	
0.484	33.16	19.98	6.848	2.478	1.666	0.411	
0.516	23.45	15.61	5.421	2.105	1.418	0.3507	
0.548	20.04	10.89	5.327	2.056	1.388	0.3436	
0.581	17.26	10.55	3.254	1.197	0.8172	0.2033	
0.613	14.47	8.356	3.207	1.197	0.8082	0.2007	
0.645	9.51	5.707	2.796	1.182	0.8029	0.1996	
0.677	8.807	5.699	2.698	1.04	0.7066	0.1757	
0.710	8.6	5.214	2.063	0.8316	0.5768	0.1433	
0.742	8.165	4.917	2.003	0.7804	0.5369	0.1337	
0.774	7.115	4.24	1.881	0.7301	0.5011	0.1247	
0.806	6.795	3.948	1.645	0.6236	0.4356	0.1087	
0.839	3.926	2.189	0.9584	0.5296	0.3705	0.09264	
0.871	1.522	0.8815	0.412	0.2074	0.1481	0.03762	
0.903	1.271	0.7705	0.3083	0.2051	0.146	0.0369	
0.935	1.259	0.6995	0.2399	0.1381	0.1037	0.02684	
0.968	0.671	0.4052	0.2048	0.08628	0.05768	0.0145	
0.100	171.3	93.537	28.979	10.2296	6.8476	1.6857	
Average of yearly averages:						0.7283	

Copied from Mebr_EECs_CAM4_v2.xls.

C.3.1. Input assumptions for California, Grape scenario.

Data used for this run:				
Output File: CA_P				
Metfile:	w93193.dvf			
PRZM scenario:	CAgrapesC.txt			
EXAMS environment file:	pond298.exv			
Chemical Name:	MB			
Description	Variable Name	Value	Units	Comments
Molecular weight	mwt	94.94	g/mol	
Henry's Law Const.	henry	0.007	atm-m ³ /mol	
Vapor Pressure	vapr	1620	torr	
Solubility	sol	15200	mg/L	
Kd	Kd		mg/L	
Koc	Koc	18	mg/L	
Photolysis half-life	kdp	9	days	Half-life
Aerobic Aquatic Metabolism	kbacw	15	days	Halfife
Anaerobic Aquatic Metabolism	kbacs		days	Halfife
Aerobic Soil Metabolism	asm	22	days	Halfife
Hydrolysis:	pH 7	11	days	Half-life
Method:	CAM	4	integer	See PRZM manual
Incorporation Depth:	DEPI	25	cm	
Application Rate:	TAPP	448	kg/ha	
Application Efficiency:	APPEFF	1	fraction	
Spray Drift	DRFT	0	fraction of application rate applied to pond	
Application Date	Date	15-1	dd/mm or dd/mm/yy or dd-mm or dd-mmm	
Record 17:	FILTRA			
	IPSCND	1		
	UPTKF			
Record 18:	PLVKRT			
	PLDKRT			
	FEXTRC	0		
Flag for Index Res. Run	IR	Pond		
Flag for runoff calc.	RUNOFF	none	none, monthly or total(average of entire run)	

Copied from Mebr_EECs_CAM4_v2.xls.

C.3.2. EECs for California, Grape scenario, sorted by year.

Year	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
1961	2.86E-01	2.05E-01	7.09E-02	2.51E-02	1.67E-02	4.13E-03
1962	6.74E-02	4.76E-02	1.72E-02	6.18E-03	4.12E-03	1.02E-03
1963	3.96E-01	2.89E-01	9.71E-02	3.43E-02	2.29E-02	5.65E-03
1964	8.80E-10	7.91E-10	5.62E-10	3.21E-10	2.29E-10	5.80E-11
1965	4.42E-05	2.86E-05	8.81E-06	3.13E-06	2.09E-06	5.15E-07
1966	3.03E-13	2.84E-13	2.17E-13	1.25E-13	8.89E-14	2.25E-14
1967	9.33E-01	6.48E-01	2.40E-01	8.56E-02	5.71E-02	1.41E-02
1968	2.02E-02	1.37E-02	4.46E-03	1.58E-03	1.05E-03	2.58E-04
1969	1.48E+01	1.09E+01	4.03E+00	1.43E+00	9.55E-01	2.35E-01
1970	1.10E+02	7.45E+01	2.57E+01	9.12E+00	6.08E+00	1.50E+00
1971	1.07E-07	1.02E-07	7.91E-08	4.59E-08	3.29E-08	8.45E-09
1972	2.98E-02	1.98E-02	6.38E-03	2.25E-03	1.50E-03	3.70E-04
1973	5.54E+00	3.75E+00	1.24E+00	4.67E-01	3.12E-01	7.68E-02
1974	3.20E-05	2.03E-05	6.06E-06	2.29E-06	1.53E-06	3.78E-07
1975	1.85E-13	1.74E-13	1.34E-13	7.64E-14	5.47E-14	1.39E-14
1976	4.59E-04	3.12E-04	1.48E-04	5.32E-05	3.55E-05	8.72E-06
1977	1.12E-07	7.18E-08	2.18E-08	7.66E-09	5.11E-09	1.26E-09
1978	6.49E+01	4.27E+01	1.35E+01	4.77E+00	3.18E+00	7.84E-01
1979	4.67E-02	3.10E-02	9.83E-03	3.46E-03	2.31E-03	5.69E-04
1980	5.58E+01	3.70E+01	1.18E+01	4.17E+00	2.78E+00	6.84E-01
1981	4.18E+00	2.83E+00	1.38E+00	4.91E-01	3.27E-01	8.07E-02
1982	8.68E-04	6.02E-04	2.17E-04	8.08E-05	5.39E-05	1.33E-05
1983	5.76E+00	4.00E+00	2.23E+00	8.15E-01	5.44E-01	1.34E-01
1984	3.68E-04	2.49E-04	8.18E-05	2.89E-05	1.93E-05	4.74E-06
1985	1.75E-03	1.22E-03	4.21E-04	1.50E-04	9.98E-05	2.46E-05
1986	1.60E+00	1.05E+00	3.34E-01	1.18E-01	7.86E-02	1.94E-02
1987	3.18E-03	2.10E-03	6.72E-04	2.43E-04	1.62E-04	3.99E-05
1988	1.81E+00	1.24E+00	4.14E-01	1.47E-01	9.81E-02	2.41E-02
1989	1.04E-02	6.54E-03	1.93E-03	7.41E-04	4.95E-04	1.22E-04
1990	4.53E-02	3.04E-02	9.90E-03	3.50E-03	2.34E-03	5.76E-04

Copied from Mebr_EECs_CAM4_v2.xls.

C.3.3. EECs for California, Grape scenario, sorted by EEC (ppb).

Sorted results						
Prob.	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
0.032	110	74.53	25.74	9.123	6.083	1.5
0.065	64.85	42.72	13.49	4.766	3.178	0.7835
0.097	55.8	37.03	11.81	4.17	2.78	0.6837
0.129	14.83	10.92	4.032	1.432	0.9547	0.2354
0.161	5.755	4.001	2.228	0.8153	0.5436	0.134
0.194	5.535	3.747	1.375	0.4907	0.3272	0.08068
0.226	4.177	2.83	1.235	0.4673	0.3116	0.07683
0.258	1.807	1.236	0.4142	0.1471	0.09807	0.02412
0.290	1.601	1.053	0.3341	0.1178	0.07857	0.01937
0.323	0.933	0.6478	0.2396	0.08564	0.0571	0.01408
0.355	0.3957	0.289	0.09714	0.03434	0.02289	0.005645
0.387	0.2863	0.2048	0.07085	0.0251	0.01673	0.004126
0.419	0.0674	0.04759	0.01724	0.006176	0.004119	0.001016
0.452	0.04668	0.03104	0.009903	0.003504	0.002336	0.000576
0.484	0.04534	0.03044	0.009831	0.003464	0.002309	0.0005694
0.516	0.02977	0.01984	0.00638	0.002254	0.001503	0.0003696
0.548	0.02022	0.01365	0.00446	0.001575	0.00105	0.0002582
0.581	0.01042	0.006543	0.00193	0.0007413	0.0004947	0.000122
0.613	0.003183	0.002104	0.0006717	0.0002425	0.0001617	3.99E-05
0.645	0.001749	0.001218	0.0004214	0.0001497	9.98E-05	2.46E-05
0.677	0.000868	0.0006023	0.000217	8.08E-05	5.39E-05	1.33E-05
0.710	0.0004585	0.0003115	0.0001483	5.32E-05	3.55E-05	8.72E-06
0.742	0.000368	0.0002487	8.18E-05	2.89E-05	1.93E-05	4.74E-06
0.774	4.42E-05	2.86E-05	8.81E-06	3.13E-06	2.09E-06	5.15E-07
0.806	3.20E-05	2.03E-05	6.06E-06	2.29E-06	1.53E-06	3.78E-07
0.839	1.12E-07	1.02E-07	7.91E-08	4.59E-08	3.29E-08	8.45E-09
0.871	1.07E-07	7.18E-08	2.18E-08	7.66E-09	5.11E-09	1.26E-09
0.903	8.80E-10	7.91E-10	5.62E-10	3.21E-10	2.29E-10	5.80E-11
0.935	3.03E-13	2.84E-13	2.17E-13	1.25E-13	8.89E-14	2.25E-14
0.968	1.85E-13	1.74E-13	1.34E-13	7.64E-14	5.47E-14	1.39E-14
0.100	51.703	34.419	11.0322	3.8962	2.59747	0.63887
Average of yearly averages:						0.11882

Copied from Mebr_EECs_CAM4_v2.xls.

C.4.1. Input assumptions for North Carolina, Tobacco scenario.

Data used for this run:				
Output File: NC_TO				
Metfile:	w13722.dvf			
PRZM scenario:	NCtobaccoC.txt			
EXAMS environment file:	pond298.exv			
Chemical Name:	MB			
Description	Variable Name	Value	Units	Comments
Molecular weight	mwt	94.94	g/mol	
Henry's Law Const.	henry	0.007	atm-m ³ /mol	
Vapor Pressure	vapr	1620	torr	
Solubility	sol	15200	mg/L	
Kd	Kd		mg/L	
Koc	Koc	18	mg/L	
Photolysis half-life	kdp	9	days	Half-life
Aerobic Aquatic Metabolism	kbacw	15	days	Half-life
Anaerobic Aquatic Metabolism	kbacs		days	Half-life
Aerobic Soil Metabolism	asm	22	days	Half-life
Hydrolysis:	pH 7	11	days	Half-life
Method:	CAM	4	integer	See PRZM manual
Incorporation Depth:	DEPI	25	cm	
Application Rate:	TAPP	959	kg/ha	
Application Efficiency:	APPEFF	1	fraction	
Spray Drift	DRFT	0	fraction of application rate applied to pond	
Application Date	Date	15-2	dd/mm or dd/mm or dd-mm or dd-mmm	
Record 17:	FILTRA			
	IPSCND	1		
	UPTKF			
Record 18:	PLVKRT			
	PLDKRT			
	FEXTRC	0		
Flag for Index Res. Run	IR	Pond		
Flag for runoff calc.	RUNOFF	none	none, monthly or total(average of entire run)	

C.4.2. EECs for North Carolina, Tobacco scenario, sorted by year.

Year	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
1961	2.75E+01	2.07E+01	7.25E+00	2.56E+00	1.71E+00	4.21E-01
1962	1.75E+00	1.15E+00	4.84E-01	1.79E-01	1.20E-01	2.95E-02
1963	2.22E+00	1.46E+00	4.88E-01	1.86E-01	1.24E-01	3.07E-02
1964	2.15E+02	1.47E+02	4.95E+01	1.75E+01	1.16E+01	2.86E+00
1965	1.25E+00	8.05E-01	2.55E-01	9.07E-02	6.05E-02	1.50E-02
1966	4.65E+01	3.19E+01	1.14E+01	4.09E+00	2.72E+00	6.72E-01
1967	1.35E+01	8.72E+00	3.01E+00	1.06E+00	7.09E-01	1.75E-01
1968	9.37E-02	5.59E-02	1.83E-02	8.91E-03	6.03E-03	1.55E-03
1969	9.38E-01	6.04E-01	2.62E-01	1.00E-01	6.67E-02	1.65E-02
1970	3.19E+01	2.19E+01	6.92E+00	2.44E+00	1.63E+00	4.02E-01
1971	2.73E+00	1.66E+00	4.69E-01	1.67E-01	1.11E-01	2.75E-02
1972	2.12E-02	1.33E-02	3.89E-03	2.03E-03	1.40E-03	4.63E-04
1973	1.19E+00	7.47E-01	2.95E-01	1.09E-01	7.30E-02	1.80E-02
1974	5.45E+00	3.59E+00	1.60E+00	5.71E-01	3.81E-01	9.41E-02
1975	1.16E+00	8.56E-01	2.81E-01	1.03E-01	6.87E-02	1.70E-02
1976	5.87E-02	3.62E-02	1.40E-02	5.00E-03	3.63E-03	8.96E-04
1977	9.72E-01	6.43E-01	3.00E-01	1.11E-01	7.43E-02	1.84E-02
1978	9.12E-01	5.83E-01	2.32E-01	8.61E-02	5.76E-02	1.43E-02
1979	3.28E+01	2.71E+01	1.55E+01	5.59E+00	3.73E+00	9.20E-01
1980	2.25E+02	1.55E+02	5.27E+01	1.87E+01	1.25E+01	3.07E+00
1981	1.29E+01	8.42E+00	2.61E+00	9.19E-01	6.13E-01	1.51E-01
1982	3.19E+00	2.41E+00	1.12E+00	4.44E-01	2.96E-01	7.32E-02
1983	1.37E+00	8.82E-01	4.32E-01	1.71E-01	1.14E-01	2.81E-02
1984	3.69E+00	2.37E+00	9.29E-01	3.35E-01	2.23E-01	5.49E-02
1985	4.23E-01	2.77E-01	8.39E-02	2.96E-02	2.02E-02	5.14E-03
1986	2.50E-01	1.56E-01	4.85E-02	1.70E-02	1.15E-02	2.87E-03
1987	9.44E+00	6.67E+00	3.38E+00	1.20E+00	8.01E-01	1.98E-01
1988	1.27E-02	7.81E-03	2.23E-03	1.01E-03	6.88E-04	1.81E-04
1989	3.49E+01	2.26E+01	9.67E+00	3.46E+00	2.31E+00	5.69E-01
1990	3.05E+01	1.92E+01	5.72E+00	2.02E+00	1.35E+00	3.32E-01

Copied from Mebr_EECs_CAM4_v2.xls.

C.4.3. EECs for North Carolina, Tobacco scenario, sorted by EEC (ppb).

Sorted results						
Prob.	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
0.032	225	155	52.74	18.74	12.49	3.072
0.065	215	147	49.51	17.46	11.64	2.863
0.097	46.45	31.85	15.5	5.594	3.73	0.9198
0.129	34.85	27.13	11.43	4.085	2.724	0.6718
0.161	32.75	22.62	9.667	3.458	2.306	0.5685
0.194	31.91	21.89	7.252	2.56	1.707	0.421
0.226	30.53	20.65	6.924	2.442	1.628	0.4016
0.258	27.49	19.21	5.718	2.018	1.346	0.3319
0.290	13.53	8.724	3.379	1.201	0.8008	0.1975
0.323	12.92	8.421	3.01	1.062	0.7087	0.1749
0.355	9.438	6.669	2.607	0.9189	0.6127	0.1512
0.387	5.45	3.588	1.601	0.5714	0.3814	0.0941
0.419	3.686	2.413	1.118	0.4444	0.2964	0.07319
0.452	3.185	2.374	0.9294	0.3345	0.2231	0.05493
0.484	2.728	1.656	0.4875	0.186	0.124	0.0307
0.516	2.218	1.463	0.4837	0.1792	0.1195	0.02952
0.548	1.753	1.153	0.4686	0.1708	0.114	0.02811
0.581	1.371	0.8824	0.4315	0.1666	0.1113	0.02751
0.613	1.249	0.8557	0.3003	0.1114	0.07427	1.84E-02
0.645	1.189	0.8045	0.295	0.109	7.30E-02	1.80E-02
0.677	1.155	0.7465	0.281	1.03E-01	6.87E-02	1.70E-02
0.710	0.9721	0.6428	0.2621	1.00E-01	6.67E-02	1.65E-02
0.742	0.9375	0.6037	2.55E-01	9.07E-02	6.05E-02	1.50E-02
0.774	9.12E-01	5.83E-01	2.32E-01	8.61E-02	5.76E-02	1.43E-02
0.806	4.23E-01	2.77E-01	8.39E-02	2.96E-02	2.02E-02	5.14E-03
0.839	2.50E-01	1.56E-01	4.85E-02	1.70E-02	1.15E-02	2.87E-03
0.871	9.37E-02	5.59E-02	1.83E-02	8.91E-03	6.03E-03	1.55E-03
0.903	5.87E-02	3.62E-02	1.40E-02	5.00E-03	3.63E-03	8.96E-04
0.935	2.12E-02	1.33E-02	3.89E-03	2.03E-03	1.40E-03	4.63E-04
0.968	1.27E-02	7.81E-03	2.23E-03	1.01E-03	6.88E-04	1.81E-04
0.100	45.29	31.378	15.093	5.4431	3.6294	0.895
Average of yearly averages:						0.34072

Copied from Mebr_EECs_CAM4_v2.xls.

C.5.1. Input assumptions for Index Reservoir Scenario - Florida Strawberries.

Data used for this run:

Output File: FL_IR				
Metfile: w12842.dvf				
PRZM scenario: FLstrawberry.txt				
EXAMS environment file: ir298.exv				
Chemical Name: MB				
Description	Variable Name	Value	Units	Comments
Molecular weight	mwt	94.94	g/mol	
Henry's Law Const.	henry	0.007	atm-m ³ /mol	
Vapor Pressure	vapr	1620	torr	
Solubility	sol	15200	mg/L	
Kd	Kd		mg/L	
Koc	Koc	18	mg/L	
Photolysis half-life	kdp	9	days	Half-life
Aerobic Aquatic Metabolism	kbacw	15	days	Half-life
Anaerobic Aquatic Metabolism	kbacs		days	Half-life
Aerobic Soil Metabolism	asm	22	days	Half-life
Hydrolysis:	pH 7	11	days	Half-life
Method:	CAM	4	integer	See PRZM manual
Incorporation Depth:	DEPI	25	cm	
Application Rate:	TAPP	448	kg/ha	
Application Efficiency:	APPEFF	1	fraction	
Spray Drift	DRFT	0	fraction of application rate applied to pond	
Application Date	Date	15-8	dd/mm or dd/mmm or dd-mm or dd-mmm	
Record 17:	FILTRA			
	IPSCND	1		
	UPTKF			
Record 18:	PLVKRT			
	PLDKRT			
	FEXTRC	0		
Flag for Index Res. Run	IR	IR		
Flag for runoff calc.	RUNOFF	total	none, monthly or total(average of entire run)	

Copied from Mebr_EECs_CAM4_v2.xls.

C.5.2. EDWCs (ppb) for Index Reservoir Scenario - Florida Strawberries, sorted by year.

Year	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
1961	1.90E+02	8.54E+01	2.03E+01	7.25E+00	4.86E+00	1.20E+00
1962	4.14E+01	1.67E+01	7.65E+00	2.96E+00	1.99E+00	4.93E-01
1963	4.80E+01	1.91E+01	4.70E+00	1.73E+00	1.18E+00	2.94E-01
1964	7.52E+01	4.24E+01	1.30E+01	4.79E+00	3.23E+00	7.96E-01
1965	3.02E+00	1.18E+00	4.48E-01	3.06E-01	2.14E-01	5.41E-02
1966	3.64E+00	1.48E+00	3.70E-01	1.88E-01	1.42E-01	3.68E-02
1967	1.96E+01	1.01E+01	2.86E+00	1.09E+00	7.52E-01	1.87E-01
1968	1.71E+01	6.66E+00	2.84E+00	1.15E+00	8.04E-01	1.99E-01
1969	1.24E+02	6.20E+01	1.53E+01	5.55E+00	3.72E+00	9.20E-01
1970	2.42E+02	9.31E+01	2.24E+01	8.01E+00	5.37E+00	1.33E+00
1971	1.66E+03	6.84E+02	1.44E+02	5.11E+01	3.41E+01	8.42E+00
1972	2.59E+02	1.38E+02	4.02E+01	1.42E+01	9.47E+00	2.33E+00
1973	4.67E+01	2.77E+01	7.69E+00	2.93E+00	1.98E+00	4.89E-01
1974	3.05E+00	1.35E+00	5.96E-01	3.01E-01	2.16E-01	5.47E-02
1975	8.79E+00	3.56E+00	1.45E+00	7.54E-01	5.27E-01	1.32E-01
1976	2.45E+02	1.25E+02	2.68E+01	9.63E+00	6.44E+00	1.59E+00
1977	4.22E+02	1.63E+02	3.61E+01	1.28E+01	8.53E+00	2.11E+00
1978	1.11E+02	4.42E+01	9.67E+00	3.52E+00	2.37E+00	5.86E-01
1979	7.81E+01	4.23E+01	1.31E+01	5.03E+00	3.37E+00	8.35E-01
1980	5.36E+02	2.06E+02	4.71E+01	1.66E+01	1.11E+01	2.73E+00
1981	3.20E+01	1.48E+01	3.81E+00	1.46E+00	9.92E-01	2.47E-01
1982	1.29E+02	6.53E+01	1.57E+01	5.94E+00	3.99E+00	9.85E-01
1983	1.63E+01	7.05E+00	3.91E+00	1.60E+00	1.08E+00	2.68E-01
1984	8.13E+01	3.33E+01	9.05E+00	3.27E+00	2.19E+00	5.41E-01
1985	1.88E+01	8.87E+00	2.38E+00	8.99E-01	6.27E-01	1.56E-01
1986	1.23E+02	4.75E+01	1.26E+01	4.54E+00	3.05E+00	7.53E-01
1987	2.28E+01	8.67E+00	2.57E+00	9.95E-01	6.83E-01	1.70E-01
1988	3.02E+02	1.18E+02	2.91E+01	1.11E+01	7.41E+00	1.82E+00
1989	2.06E+01	8.51E+00	4.38E+00	1.59E+00	1.08E+00	2.68E-01
1990	1.61E+00	6.89E-01	2.84E-01	1.19E-01	7.92E-02	1.99E-02

Copied from Mebr_EECs_CAM4_v2.xls.

C.5.3. EDWCs for Index Reservoir Scenario - Florida Stawberries, sorted by EDWC (ppb).

Sorted results						
Prob.	Peak	96 hr	21 Day	60 Day	90 Day	Yearly
0.032	1.66E+03	6.84E+02	1.44E+02	5.11E+01	3.41E+01	8.42E+00
0.065	5.36E+02	2.06E+02	4.71E+01	1.66E+01	1.11E+01	2.73E+00
0.097	4.22E+02	1.63E+02	4.02E+01	1.42E+01	9.47E+00	2.33E+00
0.129	3.02E+02	1.38E+02	3.61E+01	1.28E+01	8.53E+00	2.11E+00
0.161	2.59E+02	1.25E+02	2.91E+01	1.11E+01	7.41E+00	1.82E+00
0.194	2.45E+02	1.18E+02	2.68E+01	9.63E+00	6.44E+00	1.59E+00
0.226	2.42E+02	9.31E+01	2.24E+01	8.01E+00	5.37E+00	1.33E+00
0.258	1.90E+02	8.54E+01	2.03E+01	7.25E+00	4.86E+00	1.20E+00
0.290	1.29E+02	6.53E+01	1.57E+01	5.94E+00	3.99E+00	9.85E-01
0.323	1.24E+02	6.20E+01	1.53E+01	5.55E+00	3.72E+00	9.20E-01
0.355	1.23E+02	4.75E+01	1.31E+01	5.03E+00	3.37E+00	8.35E-01
0.387	1.11E+02	4.42E+01	1.30E+01	4.79E+00	3.23E+00	7.96E-01
0.419	8.13E+01	4.24E+01	1.26E+01	4.54E+00	3.05E+00	7.53E-01
0.452	7.81E+01	4.23E+01	9.67E+00	3.52E+00	2.37E+00	5.86E-01
0.484	7.52E+01	3.33E+01	9.05E+00	3.27E+00	2.19E+00	5.41E-01
0.516	4.80E+01	2.77E+01	7.69E+00	2.96E+00	1.99E+00	4.93E-01
0.548	4.67E+01	1.91E+01	7.65E+00	2.93E+00	1.98E+00	4.89E-01
0.581	4.14E+01	1.67E+01	4.70E+00	1.73E+00	1.18E+00	2.94E-01
0.613	3.20E+01	1.48E+01	4.38E+00	1.60E+00	1.08E+00	2.68E-01
0.645	2.28E+01	1.01E+01	3.91E+00	1.59E+00	1.08E+00	2.68E-01
0.677	2.06E+01	8.87E+00	3.81E+00	1.46E+00	9.92E-01	2.47E-01
0.710	1.96E+01	8.67E+00	2.86E+00	1.15E+00	8.04E-01	1.99E-01
0.742	1.88E+01	8.51E+00	2.84E+00	1.09E+00	7.52E-01	1.87E-01
0.774	1.71E+01	7.05E+00	2.57E+00	9.95E-01	6.83E-01	1.70E-01
0.806	1.63E+01	6.66E+00	2.38E+00	8.99E-01	6.27E-01	1.56E-01
0.839	8.79E+00	3.56E+00	1.45E+00	7.54E-01	5.27E-01	1.32E-01
0.871	3.64E+00	1.48E+00	5.96E-01	3.06E-01	2.16E-01	5.47E-02
0.903	3.05E+00	1.35E+00	4.48E-01	3.01E-01	2.14E-01	5.41E-02
0.935	3.02E+00	1.18E+00	3.70E-01	1.88E-01	1.42E-01	3.68E-02
0.968	1.61E+00	6.89E-01	2.84E-01	1.19E-01	7.92E-02	1.99E-02
0.100	4.10E+02	1.61E+02	3.98E+01	1.40E+01	9.38E+00	2.31E+00
Average of yearly averages:						1.00E+00

Copied from Mebr_EECs_CAM4_v2.xls.

C.6. Calculation of 1-in-10 year EEC using Weibull Probability Plots.

Output from the PRZM/EXAMS simulation is typically a series of estimated environmental concentrations (EEC) corresponding to multiple years of meteorological data. Each value is an estimate of the peak concentrations corresponding to a specific averaging time (e.g., 96 hours, 21 days, etc.). The 24-hour averaging time is sometimes referred to as the "Peak" concentration because the shortest time-step for a PRZM/EXAMS simulations is one day. Therefore, the column of EEC values reported in an output file for "Peak" refers to the maximum 24-hour EEC for each of the meteorological years.

For ecological risk assessment, it is important to match the averaging time to the duration of the toxicity study. However, of the multiple years of data, which EEC should be selected in the calculation of the RQ? The most conservative case would be to choose the maximum EEC for each averaging time. An alternative would be to calculate an upper end value that is less than the maximum. One statistic adopted by OPP for use in ecological risk assessment is the 1-in-10 year return value. This is the EEC that, on average, will be exceeded only once every 10 years. It is important to note that for any single 10-year period, the 1-in-10 year value may be exceeded more than once, or not at all. The key concept is that it represents the average probability of exceedance.

The 1-in-10 year statistic can be calculated using probability plotting methods. There are a number of different techniques, but a common practice in hydrology for plotting flow-duration and flood-frequency curves is to use the plotting position associated with the Weibull distribution (Helsel and Hirsch 1993). The general formula for probability plotting is given by:

$$p = \frac{i-a}{n+1-2a}$$

where p is the probability level, n is the number of data points, and a is a coefficient that varies between 0 and 0.5. For the Weibull distribution, a is 0 so the plotting position is

$$p = \frac{i}{n+1}$$

For the PRZM/EXAMS simulations presented above, there are 30 years of meteorological data, so $n = 30$. To generate a Weibull probability plot to estimate the exceedance probabilities, the data should be sorted in descending order. That is, there is a lower probability of exceeding the maximum EEC than the second highest EEC. The plotting position associated with the maximum value is then calculated as follows:

$$p_1 = \frac{1}{30+1} = 0.03226$$

The minimum and maximum probability values associated with the entire data set will approach $[0, 1]$ as the sample size increases. Sometimes probability plots are used to estimate the values

beyond the observed range. To calculate the 1-in-10 year statistic, we need the EEC associated with a probability value of 0.100. This value does not correspond directly with any of the modeled values, but it is between third highest value ($p = 0.097$) and fourth highest value (0.129). An interpolation procedure is needed to estimate the EEC associated with $p = 0.100$. A linear interpolation is commonly performed, although two methods are available. One method involves fitting a line to the entire set of data plotted on a Weibull probability plot. The second method involves a linear interpolation only between the two values that encompass the desired p-value. PRZM/EXAMS output is based on the Weibull plotting positions with a straight line interpolation between just the two data values that encompass the desired p-value of 0.100.

C.7. FIRST Generated EDWCs (ppm) for Bromide Ion in the Standard Mississippi Pond Scenarios - Tobacco.

RUN No. 1 FOR Bromide Ion		ON Tobacco		* INPUT VALUES *			
RATE (#/AC) ONE (MULT)	No.APPS & INTERVAL	SOIL Koc	SOLUBIL (PPM)	APPL TYPE (%DRIFT)	%CROPPED AREA	INCRP (IN)	
575.000 (575.000)	1 1		.015200.0	GRANUL (.0)	6.0	

FIELD AND RESERVOIR HALFLIFE VALUES (DAYS)

METABOLIC (FIELD)	DAYS UNTIL RAIN/RUNOFF	HYDROLYSIS (RESERVOIR)	PHOTOLYSIS (RES.-EFF)	METABOLIC (RESER.)	COMBINED (RESER.)
.00	2	N/A	.00-	.00	.00

UNTREATED WATER CONC (MILLIGRAMS/LITER (PPM)) Ver 1.0 AUG 1, 2001

PEAK DAY (ACUTE) CONCENTRATION	ANNUAL AVERAGE (CHRONIC) CONCENTRATION
8.748	6.273

C.8. GENEEC Generated EECs (ppm) for Bromide Ion in the Standard Mississippi Pond Scenarios - Tobacco.

RUN No. 1 FOR Bromide ion		ON Tobacco		* INPUT VALUES *		
RATE (#/AC) ONE (MULT)	No.APPS & INTERVAL	SOIL Koc	SOLUBIL (PPM)	APPL TYPE (%DRIFT)	NO-SPRAY (FT)	INCRP (IN)
575.000 (575.000)	1 1		0.0 15200.0	GRANUL (0.0)	6.0

FIELD AND STANDARD POND HALFLIFE VALUES (DAYS)

METABOLIC (FIELD)	DAYS UNTIL RAIN/RUNOFF	HYDROLYSIS (POND)	PHOTOLYSIS (POND-EFF)	METABOLIC (POND)	COMBINED (POND)
.00	2	N/A	.00-	.00	.00

GENERIC EECs (IN MILLIGRAMS/LITER (PPM)) Version 2.0 Aug 1, 2001

PEAK GEEC	MAX 4 DAY AVG GEEC	MAX 21 DAY AVG GEEC	MAX 60 DAY AVG GEEC	MAX 90 DAY AVG GEEC
5.38	5.38	5.38	5.38	5.38

Appendix D:
Groundwater (GW) and Surface water (SW) Concentrations of Methyl Bromide and Bromide, United States Geological
Survey National Water Quality Assessment(USGS NAWQA).

Chemical	Sample Type	State	County	HUC code	Land Use Code	Sampling Date and Time	Concentration	Units
Methyl Bromide	GW	IOWA	BENTON		URBAN	21-Jul-97 09:39 AM	0.0400	ug/L
Methyl Bromide	GW	SOUTH CAROLINA	RICHLAND		URBAN	03-Oct-96 09:00 AM	0.1000	ug/L
Bromide ion	GW	ALABAMA	HOUSTON		AG	07-Mar-02 12:00 PM	0.0256	mg/L
Bromide ion	GW	BRITISH COLUMBIA	UNSPECIFIED		AG	17-Sep-02 02:10 PM	0.0188	mg/L
Bromide ion	GW	CALIFORNIA	BUTTE		OTHER	11-Sep-02 02:10 PM	0.0263	mg/L
Bromide ion	GW	CALIFORNIA	KERN		MIXED	13-Aug-02 03:30 PM	0.0264	mg/L
Bromide ion	GW	CALIFORNIA	MERCED		MIXED	21-Aug-02 12:00 PM	0.0270	mg/L
Bromide ion	GW	CALIFORNIA	RIVERSIDE		OTHER	25-May-01 12:25 PM	0.7657	mg/L
Bromide ion	GW	CALIFORNIA	RIVERSIDE		OTHER	25-May-01 01:40 PM	0.3644	mg/L
Bromide ion	GW	CALIFORNIA	RIVERSIDE		OTHER	25-May-01 05:00 PM	0.2330	mg/L
Bromide ion	GW	CALIFORNIA	RIVERSIDE		OTHER	25-May-01 10:05 PM	0.1370	mg/L
Bromide ion	GW	CALIFORNIA	RIVERSIDE		OTHER	31-May-01 07:50 PM	0.1454	mg/L
Bromide ion	GW	CALIFORNIA	STANISLAUS		AG	25-Oct-01 09:50 AM	0.0228	mg/L
Bromide ion	GW	CONNECTICUT	HARTFORD		MIXED	10-Jun-02 12:00 PM	0.0174	mg/L
Bromide ion	GW	CONNECTICUT	HARTFORD		MIXED	13-Jun-02 12:00 PM	0.0276	mg/L
Bromide ion	GW	CONNECTICUT	HARTFORD		MIXED	29-Jul-02 12:00 PM	0.0240	mg/L
Bromide ion	GW	CONNECTICUT	NEW HAVEN		MIXED	25-Jul-02 12:00 PM	0.0224	mg/L
Bromide ion	GW	CONNECTICUT	NEW LONDON		MIXED	30-Jul-02 12:00 PM	0.0274	mg/L
Bromide ion	GW	CONNECTICUT	WINDHAM		MIXED	18-Sep-02 12:00 PM	0.0264	mg/L
Bromide ion	GW	FLORIDA	ALACHUA		MIXED	19-Jun-02 11:00 AM	0.0176	mg/L
Bromide ion	GW	FLORIDA	CITRUS		MIXED	21-Aug-02 11:00 AM	0.0190	mg/L
Bromide ion	GW	FLORIDA	COLUMBIA		MIXED	18-Jun-02 11:40 AM	0.0202	mg/L
Bromide ion	GW	FLORIDA	GILCHRIST		MIXED	09-Sep-02 06:30 PM	0.0222	mg/L
Bromide ion	GW	FLORIDA	HERNANDO		MIXED	21-Aug-02 03:00 PM	0.0277	mg/L
Bromide ion	GW	FLORIDA	HILLSBOROUGH		URBAN	13-Jun-02 02:00 PM	0.0156	mg/L

Bromide ion	GW	FLORIDA	LAFAYETTE	MIXED	29-Aug-02 12:00 PM	0.0261	mg/L
Bromide ion	GW	FLORIDA	LAKE	MIXED	22-Jul-02 02:30 PM	0.0271	mg/L
Bromide ion	GW	FLORIDA	LEON	MIXED	10-Jun-02 11:00 AM	0.0231	mg/L
Bromide ion	GW	FLORIDA	LEVY	MIXED	28-Aug-02 11:00 AM	0.0274	mg/L
Bromide ion	GW	FLORIDA	MADISON	MIXED	12-Jun-02 01:30 PM	0.0249	mg/L
Bromide ion	GW	FLORIDA	MADISON	MIXED	26-Jun-02 10:10 AM	0.0225	mg/L
Bromide ion	GW	FLORIDA	MADISON	MIXED	11-Sep-02 01:00 PM	0.0236	mg/L
Bromide ion	GW	FLORIDA	MARION	MIXED	14-Aug-02 02:40 PM	0.0217	mg/L
Bromide ion	GW	FLORIDA	MARION	MIXED	22-Aug-02 11:10 AM	0.0223	mg/L
Bromide ion	GW	FLORIDA	PUTNAM	MIXED	25-Jul-02 12:30 PM	0.0242	mg/L
Bromide ion	GW	FLORIDA	SUMTER	MIXED	21-Aug-02 11:00 AM	0.0243	mg/L
Bromide ion	GW	FLORIDA	SUMTER	MIXED	22-Aug-02 11:00 AM	0.0187	mg/L
Bromide ion	GW	FLORIDA	SUWANNEE	MIXED	28-Aug-02 04:00 PM	0.0232	mg/L
Bromide ion	GW	FLORIDA	SUWANNEE	MIXED	10-Sep-02 11:40 AM	0.0231	mg/L
Bromide ion	GW	FLORIDA	SUWANNEE	MIXED	10-Sep-02 01:30 PM	0.0246	mg/L
Bromide ion	GW	FLORIDA	TAYLOR	MIXED	09-Sep-02 12:20 PM	0.0204	mg/L
Bromide ion	GW	FLORIDA	TAYLOR	MIXED	12-Sep-02 12:30 PM	0.0160	mg/L
Bromide ion	GW	FLORIDA	VOLUSIA	MIXED	23-Jul-02 03:10 PM	0.0163	mg/L
Bromide ion	GW	FLORIDA	VOLUSIA	MIXED	24-Jul-02 10:20 AM	0.0259	mg/L
Bromide ion	GW	FLORIDA	WAKULLA	MIXED	04-Jun-02 02:30 PM	0.0234	mg/L
Bromide ion	GW	GEORGIA	BAKER	AG	08-Apr-02 05:00 PM	0.0234	mg/L
Bromide ion	GW	GEORGIA	BAKER	MIXED	24-Sep-02 05:00 PM	0.0188	mg/L
Bromide ion	GW	GEORGIA	BAKER	MIXED	25-Sep-02 02:00 PM	0.0224	mg/L
Bromide ion	GW	GEORGIA	CALHOUN	AG	23-Apr-02 12:00 PM	0.0168	mg/L
Bromide ion	GW	GEORGIA	CALHOUN	MIXED	28-Aug-02 11:00 AM	0.0270	mg/L
Bromide ion	GW	GEORGIA	COOK	OTHER	19-Mar-02 01:30 PM	0.0169	mg/L
Bromide ion	GW	GEORGIA	COOK	OTHER	19-Mar-02 03:10 PM	0.0158	mg/L
Bromide ion	GW	GEORGIA	CRISP	AG	27-Mar-02 10:20 AM	0.0187	mg/L
Bromide ion	GW	GEORGIA	DOUGHERTY	AG	09-Apr-02 05:00 PM	0.0167	mg/L
Bromide ion	GW	GEORGIA	DOUGHERTY	MIXED	26-Aug-02 06:00 PM	0.0247	mg/L
Bromide ion	GW	GEORGIA	DOUGHERTY	MIXED	24-Sep-02 11:00 AM	0.0219	mg/L
Bromide ion	GW	GEORGIA	EARLY	AG	06-Mar-02 03:00 PM	0.0280	mg/L
Bromide ion	GW	GEORGIA	EARLY	MIXED	28-Aug-02 07:00 PM	0.0235	mg/L
Bromide ion	GW	GEORGIA	IRWIN	AG	05-Mar-02 12:10 PM	0.0267	mg/L
Bromide ion	GW	GEORGIA	LEE	AG	18-Mar-02 12:00 PM	0.0157	mg/L

Bromide ion	GW	GEORGIA	LEE	MIXED	27-Aug-02 10:00 AM	0.0254	mg/L
Bromide ion	GW	GEORGIA	LOWNDES	MIXED	12-Jun-02 10:30 AM	0.0174	mg/L
Bromide ion	GW	GEORGIA	MILLER	AG	05-Mar-02 02:00 PM	0.0157	mg/L
Bromide ion	GW	GEORGIA	MILLER	OTHER	21-Mar-02 04:00 PM	0.0229	mg/L
Bromide ion	GW	GEORGIA	MILLER	AG	22-Apr-02 05:00 PM	0.0224	mg/L
Bromide ion	GW	GEORGIA	MILLER	MIXED	23-Sep-02 07:00 PM	0.0214	mg/L
Bromide ion	GW	GEORGIA	MITCHELL	AG	10-Apr-02 12:00 PM	0.0162	mg/L
Bromide ion	GW	GEORGIA	MITCHELL	MIXED	29-Aug-02 12:00 PM	0.0206	mg/L
Bromide ion	GW	GEORGIA	MITCHELL	MIXED	25-Sep-02 10:00 AM	0.0250	mg/L
Bromide ion	GW	GEORGIA	RANDOLPH	AG	06-Mar-02 11:00 AM	0.0199	mg/L
Bromide ion	GW	GEORGIA	SEMINOLE	MIXED	23-Sep-02 02:00 PM	0.0286	mg/L
Bromide ion	GW	GEORGIA	SUMTER	AG	04-Mar-02 11:00 AM	0.0219	mg/L
Bromide ion	GW	GEORGIA	SUMTER	AG	22-Mar-02 12:00 PM	0.0253	mg/L
Bromide ion	GW	GEORGIA	TURNER	AG	27-Mar-02 12:45 PM	0.0260	mg/L
Bromide ion	GW	GEORGIA	TURNER	AG	10-Apr-02 10:50 AM	0.0234	mg/L
Bromide ion	GW	GEORGIA	WORTH	AG	28-Feb-02 09:50 AM	0.0286	mg/L
Bromide ion	GW	GEORGIA	WORTH	AG	16-Apr-02 10:15 AM	0.0182	mg/L
Bromide ion	GW	IDAHO	JEROME	AG	19-Jun-02 10:00 AM	0.0233	mg/L
Bromide ion	GW	IDAHO	LINCOLN	AG	19-Jun-02 02:00 PM	0.0208	mg/L
Bromide ion	GW	INDIANA	DELAWARE	AG	11-Sep-02 04:00 PM	0.0287	mg/L
Bromide ion	GW	INDIANA	HAMILTON	AG	04-Sep-02 06:00 PM	0.0221	mg/L
Bromide ion	GW	INDIANA	HANCOCK	AG	09-Aug-02 10:30 AM	0.0206	mg/L
Bromide ion	GW	INDIANA	HENDRICKS	AG	03-Sep-02 05:00 PM	0.0222	mg/L
Bromide ion	GW	INDIANA	HENDRICKS	AG	04-Sep-02 10:30 AM	0.0237	mg/L
Bromide ion	GW	INDIANA	NEWTON	AG	13-Jun-02 11:00 AM	0.0244	mg/L
Bromide ion	GW	INDIANA	SHELBY	AG	06-Aug-02 12:00 PM	0.0154	mg/L
Bromide ion	GW	IOWA	LINN	AG	26-Aug-02 01:00 PM	0.0268	mg/L
Bromide ion	GW	IOWA	POLK	MIXED	28-Aug-02 12:15 PM	0.0349	mg/L
Bromide ion	GW	MARYLAND	DORCHESTER	AG	10-Oct-01 11:00 AM	0.0204	mg/L
Bromide ion	GW	MARYLAND	SOMERSET	MIXED	01-Nov-01 12:00 PM	0.0163	mg/L
Bromide ion	GW	MARYLAND	WASHINGTON	AG	06-Jun-02 09:45 AM	0.0163	mg/L
Bromide ion	GW	MARYLAND	WASHINGTON	AG	13-Jun-02 08:50 AM	0.0234	mg/L
Bromide ion	GW	MARYLAND	WASHINGTON	AG	13-Jun-02 02:30 PM	0.0206	mg/L
Bromide ion	GW	MASSACHUSETTS	HAMPDEN	MIXED	27-Aug-02 12:00 PM	0.0281	mg/L
Bromide ion	GW	MASSACHUSETTS	HAMPDEN	MIXED	28-Aug-02 12:00 PM	0.0209	mg/L

Bromide ion	GW	MICHIGAN	DELTA	MIXED	13-Jun-02 10:00 AM	0.0281	mg/L
Bromide ion	GW	MICHIGAN	HILLSDALE	MIXED	29-Aug-02 11:00 AM	0.0282	mg/L
Bromide ion	GW	MINNESOTA	CASS	OTHER	22-Jul-02 02:30 PM	0.0169	mg/L
Bromide ion	GW	MISSOURI	GREENE	AG	17-May-02 01:00 PM	0.0252	mg/L
Bromide ion	GW	NEBRASKA	ANTELOPE	MIXED	29-Jul-02 09:00 AM	0.0258	mg/L
Bromide ion	GW	NEBRASKA	BROWN	MIXED	07-Aug-02 03:00 PM	0.0231	mg/L
Bromide ion	GW	NEBRASKA	BUFFALO	MIXED	16-Jul-02 01:00 PM	0.0268	mg/L
Bromide ion	GW	NEBRASKA	CHASE	OTHER	04-Sep-02 10:00 AM	0.0262	mg/L
Bromide ion	GW	NEBRASKA	CUSTER	MIXED	21-Aug-02 01:00 PM	0.0274	mg/L
Bromide ion	GW	NEBRASKA	CUSTER	MIXED	23-Aug-02 12:00 PM	0.0216	mg/L
Bromide ion	GW	NEBRASKA	HOWARD	MIXED	22-Aug-02 02:00 PM	0.0258	mg/L
Bromide ion	GW	NEBRASKA	PIERCE	MIXED	30-Jul-02 09:00 AM	0.0278	mg/L
Bromide ion	GW	NEBRASKA	VALLEY	MIXED	25-Aug-02 04:00 PM	0.0223	mg/L
Bromide ion	GW	NEVADA	CARSON CITY	URBAN	23-Apr-02 10:35 AM	0.0155	mg/L
Bromide ion	GW	NEVADA	CARSON CITY	URBAN	08-May-02 10:00 AM	0.0210	mg/L
Bromide ion	GW	NEVADA	CARSON CITY	URBAN	22-May-02 10:15 AM	0.0201	mg/L
Bromide ion	GW	NEVADA	CARSON CITY	URBAN	28-May-02 11:45 AM	0.0225	mg/L
Bromide ion	GW	NEVADA	CARSON CITY	URBAN	04-Jun-02 10:40 AM	0.0255	mg/L
Bromide ion	GW	NEVADA	WASHOE	URBAN	05-Jun-02 12:00 PM	0.0158	mg/L
Bromide ion	GW	NEW HAMPSHIRE	GRAFTON	MIXED	10-Sep-02 12:00 PM	0.0166	mg/L
Bromide ion	GW	NEW HAMPSHIRE	SULLIVAN	MIXED	05-Sep-02 12:00 PM	0.0222	mg/L
Bromide ion	GW	NEW JERSEY	CAMDEN	URBAN	01-Jul-02 06:00 PM	0.0265	mg/L
Bromide ion	GW	NEW JERSEY	CAMDEN	URBAN	11-Jul-02 10:00 AM	0.0227	mg/L
Bromide ion	GW	NEW JERSEY	SALEM	AG	10-Jul-02 03:00 PM	0.0283	mg/L
Bromide ion	GW	NORTH CAROLINA	CARTERET	AG	03-Apr-02 10:00 AM	0.0206	mg/L
Bromide ion	GW	NORTH CAROLINA	HYDE	AG	15-Apr-02 12:45 PM	0.0192	mg/L
Bromide ion	GW	OREGON	CLACKAMAS	MIXED	25-Jun-02 12:00 PM	0.0286	mg/L
Bromide ion	GW	OREGON	CLACKAMAS	MIXED	25-Jun-02 05:00 PM	0.0271	mg/L
Bromide ion	GW	OREGON	LINN	MIXED	08-Jul-02 01:00 PM	0.0268	mg/L
Bromide ion	GW	OREGON	YAMHILL	MIXED	12-Jul-02 01:00 PM	0.0156	mg/L
Bromide ion	GW	PENNSYLVANIA	FRANKLIN	AG	19-Jun-02 03:15 PM	0.0254	mg/L
Bromide ion	GW	SOUTH CAROLINA	BEAUFORT	MIXED	04-Jun-02 12:14 PM	0.0277	mg/L
Bromide ion	GW	SOUTH CAROLINA	COLLETON	MIXED	03-Jun-02 12:10 PM	0.0277	mg/L
Bromide ion	GW	SOUTH CAROLINA	ORANGEBURG	MIXED	22-May-02 11:30 AM	0.0162	mg/L
Bromide ion	GW	VERMONT	CALEDONIA	MIXED	22-Aug-02 12:00 PM	0.0175	mg/L

Bromide ion	GW	VERMONT	ORANGE		MIXED	21-Aug-02 12:00 PM	0.0282	mg/L
Bromide ion	GW	VIRGINIA	AUGUSTA		AG	12-Jun-02 02:45 PM	0.0175	mg/L
Bromide ion	GW	VIRGINIA	AUGUSTA		AG	13-Jun-02 12:00 PM	0.0153	mg/L
Bromide ion	GW	VIRGINIA	PAGE		AG	04-Jun-02 10:30 AM	0.0256	mg/L
Bromide ion	GW	WASHINGTON	ADAMS		AG	18-Jul-02 10:30 AM	0.0202	mg/L
Bromide ion	GW	WASHINGTON	GRANT		AG	15-Jul-02 03:00 PM	0.0187	mg/L
Bromide ion	GW	WASHINGTON	GRANT		MIXED	26-Sep-02 12:30 PM	0.0207	mg/L
Bromide ion	GW	WASHINGTON	PIERCE		URBAN	21-Aug-02 10:30 AM	0.0175	mg/L
Bromide ion	GW	WASHINGTON	PIERCE		URBAN	22-Aug-02 10:30 AM	0.0170	mg/L
Bromide ion	GW	WEST VIRGINIA	BERKELEY		AG	23-May-02 12:00 PM	0.0269	mg/L
Bromide ion	GW	WEST VIRGINIA	JEFFERSON		AG	05-Jun-02 10:30 AM	0.0260	mg/L
Bromide ion	GW	WISCONSIN	ADAMS		AG	29-Jul-02 10:00 AM	0.0263	mg/L
Bromide ion	GW	WISCONSIN	COLUMBIA		MIXED	11-Sep-02 10:00 AM	0.0157	mg/L
Bromide ion	GW	WISCONSIN	LANGLADE		AG	20-Aug-02 05:00 PM	0.0179	mg/L
Bromide ion	GW	WISCONSIN	MARATHON		AG	12-Aug-02 05:00 PM	0.0188	mg/L
Bromide ion	GW	WISCONSIN	MARQUETTE		MIXED	21-May-02 10:20 AM	0.0165	mg/L
Bromide ion	GW	WISCONSIN	MARQUETTE		AG	29-Jul-02 02:00 PM	0.0232	mg/L
Bromide ion	GW	WISCONSIN	MARQUETTE		AG	30-Jul-02 03:00 PM	0.0150	mg/L
Bromide ion	GW	WISCONSIN	OUTAGAMIE		MIXED	29-May-02 03:00 PM	0.0195	mg/L
Bromide ion	GW	WISCONSIN	POLK		MIXED	15-Jul-02 12:30 PM	0.0174	mg/L
Bromide ion	GW	WISCONSIN	PORTAGE		AG	14-Aug-02 09:00 AM	0.0164	mg/L
Bromide ion	GW	WISCONSIN	SHAWANO		MIXED	26-Jun-02 02:00 PM	0.0173	mg/L
Bromide ion	GW	WISCONSIN	SHAWANO		MIXED	27-Jun-02 11:30 AM	0.0217	mg/L
Bromide ion	GW	WISCONSIN	WAUPACA		AG	13-Aug-02 05:00 PM	0.0156	mg/L
Bromide ion	GW	WISCONSIN	WAUPACA		AG	14-Aug-02 05:00 PM	0.0236	mg/L
Bromide ion	GW	WISCONSIN	WAUPACA		AG	21-Aug-02 03:00 PM	0.0256	mg/L
Bromide ion	GW	WISCONSIN	WAUSHARA		MIXED	22-May-02 10:10 AM	0.0282	mg/L
Bromide ion	GW	WISCONSIN	WAUSHARA		AG	31-Jul-02 11:00 AM	0.0162	mg/L
Bromide ion	GW	WISCONSIN	WAUSHARA		AG	27-Aug-02 03:00 PM	0.0274	mg/L
Bromide ion	GW	WISCONSIN	WINNEBAGO		MIXED	28-May-02 10:50 AM	0.0170	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	21-May-01 11:15 PM	0.0621	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 12:15 AM	0.6234	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 01:15 AM	1.1395	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 02:05 AM	0.1595	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 02:15 AM	0.7709	mg/L

Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 03:00 AM	0.5859	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 03:05 AM	0.2002	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 03:15 AM	1.2572	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 04:00 AM	0.5099	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 04:00 AM	0.6098	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 04:15 AM	1.5077	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 04:35 AM	0.5482	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 05:05 AM	0.5632	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 05:15 AM	1.7835	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 06:00 AM	0.4602	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 06:15 AM	1.8001	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 06:30 AM	0.6497	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 06:30 AM	1.0669	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 07:00 AM	0.6473	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 07:15 AM	1.6831	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 07:30 AM	0.8294	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 07:30 AM	1.3092	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 08:15 AM	1.2333	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 08:30 AM	0.9284	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 08:30 AM	0.9932	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 09:15 AM	1.4348	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 09:30 AM	1.0777	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 09:30 AM	1.2615	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 10:15 AM	0.6323	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 10:30 AM	1.0090	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 10:30 AM	1.1138	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 11:30 AM	0.9344	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 11:30 AM	1.1784	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 12:30 PM	0.7461	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 12:30 PM	0.9512	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 01:30 PM	0.7362	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 02:30 PM	0.3672	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 03:30 PM	0.2613	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 08:00 PM	1.4328	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 09:00 PM	1.3750	mg/L

Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 10:00 PM	0.2524	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 10:00 PM	1.0415	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	22-May-01 11:00 PM	0.1944	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 11:00 PM	1.4965	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	22-May-01 11:05 PM	0.1615	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	23-May-01 12:10 AM	0.1957	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	23-May-01 01:00 AM	0.1636	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 01:00 AM	0.6303	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 01:00 AM	1.2605	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 01:30 AM	0.2114	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 02:00 AM	0.2036	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 02:00 AM	0.7127	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 02:20 AM	0.8354	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	23-May-01 03:00 AM	0.1915	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 03:00 AM	0.2552	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 03:10 AM	0.7418	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 03:30 AM	0.2271	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	23-May-01 04:00 AM	0.1472	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 04:00 AM	0.2929	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 04:00 AM	0.4563	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 04:00 AM	0.7304	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	23-May-01 05:00 AM	0.1529	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 05:00 AM	0.4684	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 05:00 AM	0.4755	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 05:00 AM	4.1988	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 06:00 AM	0.4101	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 06:00 AM	0.5474	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 06:00 AM	4.0351	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 06:20 AM	0.2218	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 07:00 AM	0.3819	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 07:00 AM	0.6659	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 07:15 AM	1.5419	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 07:20 AM	0.2311	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 08:00 AM	0.6712	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 08:05 AM	1.6773	mg/L

Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 08:20 AM	0.3391	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 09:00 AM	0.5845	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 09:00 AM	1.0049	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 09:15 AM	0.4554	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 10:00 AM	0.2871	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 10:10 AM	0.4071	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 10:15 AM	0.5364	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 11:00 AM	0.2513	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 11:00 AM	0.4352	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 11:00 AM	0.5821	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 11:15 AM	0.5285	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 12:00 PM	0.9524	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 12:15 PM	0.5727	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 01:05 PM	1.0564	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 01:15 PM	0.5287	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 02:00 PM	0.6784	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 02:15 PM	0.3898	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 03:15 PM	0.5438	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 04:15 PM	0.7542	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 05:00 PM	0.1851	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 05:40 PM	0.2361	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 06:00 PM	0.6973	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 07:00 PM	0.5010	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 08:00 PM	0.3348	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 09:00 PM	0.2936	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	23-May-01 10:00 PM	0.2460	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	24-May-01 12:00 AM	0.5852	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	OTHER	24-May-01 12:00 AM	1.4336	mg/L
Bromide ion	SW	CALIFORNIA	RIVERSIDE	18070203	MIXED	31-May-01 08:20 PM	0.1813	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	21-May-01 09:52 PM	1.9303	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	21-May-01 10:51 PM	0.3792	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	22-May-01 01:05 AM	0.4572	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	22-May-01 01:53 AM	0.0790	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	22-May-01 03:15 AM	0.0610	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	22-May-01 05:00 AM	0.0779	mg/L

Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	22-May-01 06:35 AM	0.0889	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	22-May-01 06:50 AM	0.0729	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	22-May-01 07:30 AM	15.5950	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	22-May-01 08:00 AM	0.0799	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	22-May-01 11:30 PM	0.2273	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	23-May-01 01:35 AM	0.2188	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	23-May-01 05:00 AM	0.6608	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	23-May-01 08:30 AM	0.4608	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	23-May-01 09:30 AM	0.5468	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	23-May-01 10:30 AM	1.5044	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	23-May-01 11:30 AM	0.7958	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	23-May-01 12:30 PM	0.5093	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	23-May-01 01:00 PM	0.2975	mg/L
Bromide ion	SW	CALIFORNIA	SAN BERNARDINO	18070203	OTHER	23-May-01 05:20 PM	0.1858	mg/L

**Appendix E:
Detailed Risk Quotients**

Table E1. Risk Quotients for Exposure of Mammals Using the LD₅₀/ft² Risk Assessment Method			
Mammal LD₅₀ (oral exposure)	86	mg/kg	
Application rate	4165	mg/ft ²	
	Body Weight (kg)	LD₅₀ (mg)¹	RQ³
Small	0.01 5	1.29	3229
Medium	0.03 5	3.01	1384
Large	1	86	48
¹ LD ₅₀ in mg/kg multiplied by body weight ² The exposure rate of 400 lb/acre is converted to mg/ft ² using the following conversion factors: given 43,560 square feet/acre and 453,590 mg/lb ³ To calculate risk quotients, the exposure amount in mg/ft ² is divided by the product of acute oral LD ₅₀ (mg/kg) and bird body weight (kg)			

Table E2. Risk Quotients for Exposure of Birds Using the LD₅₀/ft² Risk Assessment Method			
Bird LD₅₀ (oral exposure)	73	mg/kg	
Application rate	4165	mg/ft ²	
	Body Weight (kg)	LD₅₀ (mg)¹	RQ³
Small	0.01	0.73	5705
Medium	0.4	29.2	143
Large	4	292	14
¹ LD ₅₀ in mg/kg multiplied by body weight ² The exposure rate of 400 lb/acre is converted to mg/ft ² using the following conversion factors: given 43,560 square feet/acre and 453,590 mg/lb ³ To calculate risk quotients, the exposure amount in mg/ft ² is divided by the product of acute oral LD ₅₀ (mg/kg) and bird body weight (kg)			

Table E3. Screening-Level Acute Avian Inhalation Risk Assessment (where measured air concentrations are available)					
Data Entry					
MW chemical	94.9				
BW bird g	50				
Air conc (ppm)	27				
mammal oral LD50 (mg/kg)	86				
mammal inhalation LC50 (mg/L)	3.03				
mammal inhalation LD50 exposure duration (h)	4	Note assume 4 hours unless study indicates otherwise			
Bird oral LD50 (mg/kg)	73				
mammal to bird conversion factor (assume 3.2)	3.2				
mammal inhalation conversion factor (assume 43.5)	43.5				
Results					
Calculated mammal inhalation LD50 (mg/kg)	527.22				
Calculated bird inhalation LD50 (mg/kg)	139.8512				
Calculated air concentration in mg/m3	104.7975	((pesticide MW/(air conc. ppm)))/24.45			
Calculated Inhalation rate (cm3/hr)	5090.937				
Calculated inhalation one hour dose (mg/kg)	10.67035				
Avian Risk Quotient Calculations					
Avian Acute RQ Inhalation (estimated)	0.076298				
Number of seconds for bird inhalation dose to achieve inhalation LD50	47183.48	where 3600 is the number of seconds in the one-hour modeled exposure period			
Mammalian Risk Quotient Calculations					
pesticide air concentration (mg/L)	0.104798	1000 liters in a cubic meter			
mammal inhalation LC50 (mg/L)	3.03	from entry in B7			
Mammal Inhalation Risk Quotient	0.034587	quotient of air concentration/LC50			

Table E4. Screening-Level Acute Avian Inhalation Risk Assessment (where measured air concentrations are available)					
Data Entry					
MW chemical	94.9				
BW bird g	50				
Air conc (ppm)	9.12				
mammal oral LD50 (mg/kg)	86				
mammal inhalation LC50 (mg/L)	3.03				
mammal inhalation LD50 exposure duration (h)	4	Note assume 4 hours unless study indicates otherwise			
Bird oral LD50 (mg/kg)	73				
mammal to bird conversion factor (assume 3.2)	3.2				
mammal inhalation conversion factor (assume 43.5)	43.5				
Results					
Calculated mammal inhalation LD50 (mg/kg)	527.22				
Calculated bird inhalation LD50 (mg/kg)	139.8512				
Calculated air concentration in mg/m3	35.39828	((pesticide MW)/(air conc. ppm))/24.45			
Calculated Inhalation rate (cm3/hr)	5090.937				
Calculated inhalation one hour dose (mg/kg)	3.604209				
Avian Risk Quotient Calculations					
Avian Acute RQ Inhalation (estimated)	0.025772				
Number of seconds for bird inhalation dose to achieve inhalation LD50	139887.9	where 3600 is the number of seconds in the one-hour modeled exposure period			
Mammalian Risk Quotient Calculations					
pesticide air concentration (mg/L)	0.035398	1000 liters in a cubic meter			
mammal inhalation LC50 (mg/L)	3.03	from entry in B7			
Mammal Inhalation Risk Quotient	0.011683	quotient of air concentration/LC50			

Table E5. Risk Quotients for methyl bromide acute and chronic exposures of aquatic species

Exposure Scenario	Units	Exposure	Toxicity	Risk Quotient⁵
Fish				
acute exposure (96 hour) ¹				
CA Tomatoes	ppm	0.16	3.9	0.041
CA Grapes	ppm	0.052	3.9	0.013
FL Strawberries	ppm	0.17	3.9	0.044
NC Tobacco	ppm	0.045	3.9	0.012
chronic exposure ²				
CA Tomatoes	ppm	0.035	0.1	0.35
CA Grapes	ppm	0.011	0.1	0.11
FL Strawberries	ppm	0.029	0.1	0.29
NC Tobacco	ppm	0.015	0.1	0.15
Aquatic Invertebrates				
acute exposure (48 hour) ³				
CA Tomatoes	ppm	0.16	2.6	0.062
CA Grapes	ppm	0.052	2.6	0.020
FL Strawberries	ppm	0.17	2.6	0.066
NC Tobacco	ppm	0.045	2.6	0.017

Table E6. Risk Quotients for methyl bromide acute and chronic exposures of algae

Algae

acute exposure (24 hour)⁴

CA Tomatoes	ppm	0.16	2.2	0.073
CA Grapes	ppm	0.052	2.2	0.024
FL Strawberries	ppm	0.17	2.2	0.077
NC Tobacco	ppm	0.045	2.2	0.021

¹Based on 24 hour peak concentration using the 96-hour LC₅₀ average concentration .

²Based on 21 day time-weighted average concentration using the 1-month NOAEC.

³Based on 24 hour peak concentration using the 48-hour LC₅₀.

⁴Based on 24 hour peak concentration using the 24-hour LC₅₀.

⁵Exposure value ÷ toxicity value

Appendix F:
HED DOC. NO. 0051439. Methyl Bromide - 2nd Report of the Health Effects
Division (HED) Hazard Identification Assessment Review Committee (HIARC)

See attached file: HED Methyl Bromide HAZ ID 053201ha.002.wpd

Appendix G:

Overview of Risk Quotients (RQs)

Risk characterization integrates the results of the exposure and ecotoxicity data to evaluate the likelihood of adverse ecological effects. The means of this integration is called the quotient method. Risk quotients (RQs) are calculated by dividing exposure estimates by acute and chronic ecotoxicity values.

$$RQ = \text{EXPOSURE} / \text{TOXICITY}$$

RQs are then compared to OPP's levels of concern (LOCs). These LOCs are used by OPP to analyze potential risk to nontarget organisms and the need to consider regulatory action. The criteria indicate that a pesticide used as directed has the potential to cause adverse effects on nontarget organisms. LOCs currently address the following risk presumption categories: (1) acute risks - regulatory action may be warranted in addition to restricted use classification, (2) acute restricted use - the potential for acute risk is high, but may be mitigated through restricted use classification, (3) acute endangered species - endangered species may be adversely affected, and (4) chronic risk - the potential for chronic risk is high regulatory action may be warranted. Currently, EFED does not perform assessments for chronic risk to plants, acute or chronic risks to insects, or chronic risk from granular/bait formulations to birds or mammals.

The ecotoxicity test values (measurement endpoints) used in the acute and chronic risk quotients are derived from required studies. Examples of ecotoxicity values derived from short-term laboratory studies that assess acute effects are: (1) LC_{50} (fish and birds), (2) LD_{50} (birds and mammals), (3) EC_{50} (aquatic plants and aquatic invertebrates) and (4) EC_{25} (terrestrial plants). Examples of toxicity test effect levels derived from the results of long-term laboratory studies that assess chronic effects are: (1) LOAEL or LOAEC (birds, fish, and aquatic invertebrates) and (2) NOAEL or NOAEC (birds, fish and aquatic invertebrates). For birds, mammals, fish and aquatic invertebrates the NOAEL or NOAEC generally is used as the ecotoxicity test value in assessing chronic effects, although other values may be used when justified. Risk presumptions and the corresponding RQs and LOCs, are tabulated below.

Table F 1. Risk presumptions for terrestrial animals based on risk quotients (RQ) and levels of concern (LOC).

Risk Presumption	RQ	LOC
Birds		
Acute Risk	EEC ¹ /LC ₅₀ or LD ₅₀ /ft ² or LD ₅₀ /day ³	0.5
Acute Restricted Use	EEC/LC ₅₀ or LD ₅₀ /ft ² or LD ₅₀ /day (or LD ₅₀ < 50 mg/kg)	0.2
Acute Endangered Species	EEC/LC ₅₀ or LD ₅₀ /ft ² or LD ₅₀ /day	0.1
Chronic Risk	EEC/NOAEC	1
Wild Mammals		
Acute Risk	EEC/LC ₅₀ or LD ₅₀ /ft ² or LD ₅₀ /day	0.5
Acute Restricted Use	EEC/LC ₅₀ or LD ₅₀ /ft ² or LD ₅₀ /day (or LD ₅₀ < 50 mg/kg)	0.2
Acute Endangered Species	EEC/LC ₅₀ or LD ₅₀ /ft ² or LD ₅₀ /day	0.1
Chronic Risk	EEC/NOAEC	1

¹ abbreviation for Estimated Environmental Concentration (ppm) on avian/mammalian food items² mg/ft²³ mg of toxicant consumed/dayLD₅₀ * wt. of birdLD₅₀ * wt. of bird**Table F2. Risk presumptions for aquatic animals based on risk quotients (RQ) and levels of concern (LOC).**

Risk Presumption	RQ	LOC
Acute Risk	EEC ¹ /LC ₅₀ or EC ₅₀	0.5
Acute Restricted Use	EEC/LC ₅₀ or EC ₅₀	0.1
Acute Endangered Species	EEC/LC ₅₀ or EC ₅₀	0.05
Chronic Risk	EEC/NOAEC	1

¹ EEC = (ppm or ppb) in water**Table F3. Risk presumptions for plants based on risk quotients (RQ) and levels of concern (LOC).**

Risk Presumption	RQ	LOC
Terrestrial and Semi-Aquatic Plants		
Acute Risk	EEC ¹ /EC ₂₅	1
Acute Endangered Species	EEC/EC ₀₅ or NOAEC	1
Aquatic Plants		
Acute Risk	EEC ² /EC ₅₀	1
Acute Endangered Species	EEC/EC ₀₅ or NOAEC	1

¹ EEC = lbs ai/A² EEC = (ppb/ppm) in water